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Chapter 2: A Critical Review: The Effect of Ethanol in Gasoline on the Fate and Transport of BTEX in the Subsurface

Authors

Susan E. Powers
Stephen E. Heermann

Editors

G. Cannon*
D. Rice*

Contributors

R. Depue*
B. Clark*

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*Lawrence Livermore National Laboratory, Livermore, CA 94550

Clarkson University • Potsdam, NY 13699
Department of Civil and Environmental Engineering
W.J. Rowley Laboratories

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2.1. Overview of Processes Affecting Ethanol and Gasoline in the Subsurface

Following a spill or leak, the presence of oxygenate chemicals in gasolines can potentially impact the migration and fate of the gasoline in the subsurface. In general, public health concerns with gasoline in the subsurface arise from the presence of dissolved species (monoaromatic hydrocarbons, such as benzene, toluene, ethyl benzene, and the three isomers of xylene [BTEX]) in groundwater that could be used for drinking purposes. There are numerous processes that affect the ultimate concentrations of chemicals in groundwater (Figure 2-1). Generally, these processes include:

- Infiltration of the gasoline through the unsaturated zone of the subsurface.

- Spreading of the gasoline pool at the water table.

- Dissolution of slightly soluble species from the gasoline into the water.

- Transport of these chemicals with the groundwater towards a potential point of contact, such as a groundwater well.

Because of the differences between the hydrophobicity of standard gasoline and hydrophilicity of alcohols, the presence of alcohols in gasoline has the potential to affect each of these fate-and-transport mechanisms.

Table 2.1 summarizes the potential impacts of ethanol on mechanisms controlling the ultimate concentration of hazardous chemicals in groundwater. As summarized briefly here and documented more fully throughout this report, ethanol has the potential to increase the concentration of BTEX species in groundwater. Based on current levels of understanding, it is known that equilibrium concentrations of BTEX increase in the presence of ethanol and that losses due to adsorption and biodegradation are reduced. However, the significance of these impacts in a subsurface setting are not known and the potential impacts of many of the mechanisms and variables identified in Table 2.1 are poorly understood at the present time. Changes in the fate of gasohol and BTEX concentrations in groundwater are attributable to the cosolvent effect associated with high ethanol concentrations in the aqueous phase. Essentially, the presence of the organic ethanol molecules in the aqueous phase makes this phase less polar and therefore more compatible with organic molecules. This and other specific mechanisms and variables that have the greatest potential impact on groundwater contamination are discussed and research needs are identified in this report following a thorough review of the present state of knowledge.

2.2. Subsurface Transport of Fuel Hydrocarbons in the Presence of Ethanol

2.2.1. Overall Phase Partitioning Behavior

Standard-formulation gasolines and water are almost completely immiscible. For example, Polak and Lu (1973) measured the aqueous solubilities of 21 gasoline compounds. The reported values ranged between 0.54 milligrams per liter (mg/L) (or parts per million [ppm]) for 2,2,5-trimethylhexane at 25ºC and 1800 mg/L for benzene. Solubilities of water in gasoline compounds were reported by Polak and Lu (1973) to range between 74 mg/L for water in 2,3,4-trimethylpentane and 690 mg/L for water in benzene. The reported solubilities do not include the effects of surface-active agents or other additives to gasoline that may contain polar components in the molecular structure.

In contrast, ethanol is completely miscible in both gasoline and water at all concentrations. When ethanol is present with both gasoline and water, the phase behaviors of water and gasoline are modified in such a way that:

- Solubilities of gasoline hydrocarbons in water increase.

- Solubility of water in gasoline increases.

- Ethanol partitions preferentially into the aqueous phase.

- Interfacial tension (IFT) between the water and the gasoline phases is reduced.

When ethanol content of gasoline is increased, the mutual solubilities increase, and the IFT becomes further reduced. However, ethanol partitions less preferentially into water with the introduction of more ethanol. With a sufficiently large proportion of ethanol, gasoline and water become completely miscible with each other and merge into a single phase. Conversely, at lower ethanol concentrations, gasoline may separate into two phases if water is added to the blend. Gasoline- and water-rich phases generally merge for ethanol fractions exceeding about 70% by weight and separate when ethanol fractions fall below this value. However, as will be shown below, ethanol fractions that bound single- or two-phase behavior depend upon the composition of the gasoline and the water content.

2.2.1.1. Ternary-phase Diagrams

Ethanol partitioning and the effects of ethanol on solubility are illustrated on a ternary-phase (gasoline-water-ethanol) diagram (Figure 2-2). Note that the diagram assumes a completely mixed system that has reached equilibrium and thus ignores complex transport phenomenon that exists in the subsurface. The diagram is not intended to convey actual phase behavior in the subsurface but instead is intended to illustrate general equilibrium phase behavior that will govern phase behavior in the subsurface. Using the three axes, one can determine the overall system mass fractions of gasoline, water, and ethanol for any point on the interior. The shaded region indicates the range of water, gasoline, and ethanol fractions where the three components exist as two separate phases while the unshaded region indicates the composition range where these components exist as a single phase. The curve separating the two regions is called the binodal curve. On Figure 2-2 the binodal curve indicates that gasoline, ethanol, and water will

exist as a single phase in all relative combinations of water and gasoline provided that the ethanol present in the entire system exceeds 70% by weight.

Tie lines transect the two-phase region and join water-rich and gasoline-rich segments of the binodal curve. These tie lines indicate the equilibrium compositions of the two phases. The points connected by the lines define the composition of the water-rich phase (on the left side of the two-phase region) and the gasoline-rich phase (on the right side of the two-phase region). The preferential partitioning of ethanol into water is indicated by the downward, left-to-right slope of the tie lines.

For example, if a gasoline initially contained 10% ethanol, its composition would be indicated by point A on Figure 2-2. If that gasoline came into contact with an equal volume of water and if the gasohol and water were allowed to equilibrate, nearly all of the ethanol would migrate into the aqueous phase. At equilibrium, the gasoline-rich phase would then have a composition indicated by point A` and the water-rich phase by point B`.

2.2.1.2. Effect of System Composition

The phase behavior of ethanol is compared with that of methanol on Figure 2-3. Ternary-phase diagrams, adapted from Letcher *et al.* (1986), are shown for three-component systems comprised of water, gasoline, and an alcohol. A comparison of the ethanol and methanol systems indicates that methanol produces a smaller single-phase region than does ethanol. Thus, less water is required to cause phase separation in a gasoline containing methanol than in a gasoline containing ethanol.

Because gasoline is a highly complex mixture of alkane, cycloalkane, alkene, and aromatic compounds, changes in gasoline composition may affect the phase behavior. To illustrate this, ternary-phase diagrams for two individual components compounds found in gasoline—2,2,4-trimethylpentane (an alkane) and toluene (an aromatic hydrocarbon)—are illustrated on Figure 2-4. A lower ethanol fraction would be required for phase separation if toluene were the hydrocarbon than if 2,2,4-trimethylpentane were the hydrocarbon. Additionally, the slopes of the tie lines in Figure 2-4a indicate that ethanol partitions less preferentially into water from toluene than from 2,2,4-trimethylpentane. Assuming that toluene is representative of the general phase behavior of the aromatic hydrocarbons and that the 2,2,4-trimethylpentane represents the properties of the alkanes, cycloalkanes, and alkenes, then one could generalize that, if the fraction of aromatics in the gasoline were increased, the single-phase region would expand; and upon phase separation, the gasoline would contain slightly more ethanol. Published phase relationships for water and ethanol in combination with a number of individual gasoline components may be found in Stephenson (1992), Letcher *et al.* (1986), and Letcher and Siswana (1992).

2.2.2. Unsaturated Zone: Infiltration and Spreading at the Water Table

Gasoline typically enters the subsurface following the corrosion or rupture of storage tanks or pipelines. Relatively small-scale releases are associated with gasoline stations, construction facilities, truck rental agencies, etc. Much larger-scale releases are commonly associated with petroleum refineries, petroleum distribution centers, industrial facilities, and civilian and military airports. Following its release into the subsurface, gasoline flows predominantly downward

toward the water table in response to gravitational forces. A fraction of the gasoline is retained as lenses or films between the air and water in the unsaturated zone. Once the bulk volume of gasoline reaches the capillary fringe, gasoline spreads laterally under a combination of gravitational and capillary forces, forming a body typically characterized by a lensoidal geometry. The capillary fringe is not completely saturated with gasoline but shares the zone with residual water and possibly air. Where air, water, and gasoline coexist at a given elevation, the air predominantly fills the largest pores; the smallest pores are generally filled with water; and gasoline fills the pores of intermediate diameter.

The introduction of ethanol affects the migration and distribution of gasoline in the subsurface in two primary ways: the capillary forces are reduced, thereby changing the multiphase flow characteristics; and, the pore structure of some mineral types is altered by chemical interactions with the alcohol. Information on the specific mechanisms is summarized below although the overall importance of these factors on the net impact of ethanol-gasolines in the subsurface has not been quantified. In fact, the few major studies on the effects of oxygenated gasolines on groundwater contamination (Malcolm Pirnie, Inc., 1998; Blue Ribbon Panel [BRP], 1999) have not even addressed the potential differences in the nature of the multiphase flow process between standard gasoline formulations and ethanol gasolines.

2.2.2.1. Change in Capillary Forces and Multiphase Flow in the Presence of Ethanol

The addition of oxygenates to gasoline changes the nature of the capillary phenomena affecting gasoline infiltration and distribution at the water table because of a reduction in the surface and interfacial tensions (IFT) between the phases. Figure 2-5a illustrates the extent of decrease in these values. Much of these data were collected for real gasolines equilibrated with water and ethanol (Kowles and Powers, 1997). The "C2" gasoline is a reformulated gasoline (RFG) containing 5.8% ethanol by volume that was developed by Phillips Chemical Company and is certified for testing in California. Ethanol contents were varied by altering the gasoline-water volume ratio or by adding additional ethanol to the system.

The IFT of the C2 system decreased in an almost perfectly linear way from 26.3 dynes/cm at 0% ethanol to 7 dynes/cm at 50% ethanol—a decrease of about 75%. In contrast, neat solvents and a surrogate gasoline comprised of xylene (20% by volume) and isooctane had a much more significant decrease in the IFT with the addition of small volumes of ethanol (less than 10%) to the aqueous phase. These differences suggest that some of the other components of the C2 gasoline also strongly affect the IFT, and that surrogate mixtures of monoaromatics and alkanes are not representative surrogates for gasoline in studies of the gasoline migration and distribution at the water table.

Data for the surface tensions (liquid-air) are available for water and organic phases in the presence of ethanol. Figure 2-5b illustrates the surface tension of water after equilibration with a variety of organic phases in the presence of ethanol. The surface tension drops for all cases substantially with the increase in ethanol, although there is very little difference among the waters equilibrated with different organic phases. These results illustrate that ethanol has a much greater effect on the surface tension of water than the presence of other gasoline constituents. In contrast, surface tension of the C2 gasoline following equilibration with water and added ethanol was 19.7 ± 0.25 over a wide range of ethanol contents (Kowles and Powers, 1997). Other

researchers have also noted the same lack of change for the surface tensions of neat solvents in ternary (organic-ethanol-water) systems (e.g., Ross and Paterson, 1979). The independence of the gasoline-air surface tension can be explained by the near complete partitioning of the ethanol into the aqueous phase.

Because of the reduction in capillary force associated with the changes in interfacial and surface tensions, the height of the capillary fringe is reduced and the depth of the gasoline pool altered. The gasoline can also enter smaller pore spaces (Demond and Roberts, 1991), potentially affecting its distribution in the vadose zone and in the gasoline pool. Ostendorf *et al.* (1993) presented a model for estimating the depth of a gasoline pool based on hydrodynamics and capillary forces. The resulting equation expresses the depth in terms of the densities of the gasoline and water, nonaqueous phase liquids (NAPL) surface tension and NAPL-water IFT, maximum saturation of the mobile gasoline phase, and a parameter that characterizes the pore-size distribution (the *n* value in the capillary pressure-saturation model of van Genuchten [1980]). Assuming that this equation can also be applied to ethanol-gasoline, we can evaluate the expected trends in the depth of the gasoline pool. Variations in the density between the C2 gasoline that has been stripped of ethanol ($\rho = 0.733$ grams per milliliter [g/mL]) and C2 gasoline with 10% ethanol by volume ($\rho = 0.738$ g/mL) have an insignificant effect on the calculated depth of the pool. The maximum saturation of the mobile form of the gasoline is unknown, but it is not expected to vary substantially. With the small variations in these properties between standard gasoline and ethanol-gasoline, the Ostendorf *et al.* (1993) equation is reduced to a direct dependence of gasoline-pool depth on the NAPL-water IFT. Thus, a reduction in the IFT would result in a decrease in the thickness of the gasoline pool and a larger areal extent of the gasoline pool. No data or modeling efforts exist to predict the extent or significance of this impact.

Although these general trends are based on theory and experimental observations from other systems, few papers in the literature are available that specifically addressed the impacts of alcohols on multiphase flow processes pertinent during gasoline infiltration and spreading at the water table. Results of the most closely related studies are described below.

Researchers at the University of Waterloo (Donaldson *et al.*, 1994) conducted the most extensive study addressing the impact of alcohol as an oxygenate in gasoline on the behavior of the gasoline in the subsurface. They observed the dynamics of M85—a mixture of 85% methanol and 15% standard gasoline—infiltration and migration in both saturated and unsaturated systems. The very high alcohol content of this gasoline resulted in a change from the immiscible displacement phenomena associated with standard gasolines to a miscible displacement process. Differences in density and viscosity become more important in miscible displacement processes than IFT. Based on the unsaturated zone infiltration experiments, the behavior of the M-85 gasoline relative to the standard gasoline used for comparison can be characterized by:

- Less lateral spreading in the unsaturated zone.

- A decrease in the height of the capillary fringe, which resulted in the formation of the gasoline pool at a lower elevation (the depth of the capillary fringe returned to its original position after the methanol was flushed from the system).

- The formation of a gasoline pool at the water table with a smooth and regular geometry that was smaller in lateral extent.

- The formation of air bubbles in the area where the M-85 displaces water due to non-ideal mixing of the methanol and water that causes a reduction in the volume of the mixture.

- The formation of a "halo" of droplets of gasoline around the periphery of the gasoline pool and infiltration zone due to reduced methanol concentrations and reduction in the effective solubility of the gasoline constituents.

The formation of residual droplets of gasoline in the saturated zone is significant because it substantially increases the NAPL-water contact area for dissolution. In addition to the formation of these droplets by precipitation when the alcohol concentration drops, they can also be formed by multiphase displacement mechanisms as the water-table elevation changes. Ryan and Dhir (1996) studied the changes in hydrocarbon entrapment at the bottom of a pool as the water table fluctuates. They found that by reducing the IFT from approximately 40 to 10 dynes/cm with the addition of isopropyl alcohol, the volume of the hydrocarbon entrapped in the saturated zone was reduced from 11 to 6% of the total pore space. Thus, trends associated with the generation of these droplets are opposite depending on the mechanism involved. High alcohol concentrations tend to increase the probability of precipitation but reduce the probability that droplets are formed during multiphase displacement.

Researchers at the University of Florida at Gainesville (for example, Rao *et al.,* 1997) recently completed a large research project on the use of ethanol as a flushing agent to enhance the dissolution and recovery of NAPLs entrapped in the subsurface. Although the researchers did not investigate the multiphase flow characteristics of the NAPLs, they did make an effort to understand the effects of ethanol on the capillary forces at the capillary fringe. Jawitz *et al.* (1998) conducted miscible displacement studies, using ethanol-water solutions to displace pure water in a small, two-dimensional sandbox that represented an unconfined aquifer. The displacing fluid was introduced through an injection well rather than through the unsaturated zone. The study made two primary observations:

- The ethanol solution preferentially stayed near the top of the sandbox because of its lower density than that of clean water.

- The capillary fringe was reduced in height by approximately 50%, the same percentage as the decrease in the air-water surface tension of the ethanol solution.

The studies were limited to the miscible displacement dynamics expected with neat ethanol displacing water.

One significant effect associated with a reduction in the IFT of water in the unsaturated zone is a reduction in the field capacity. Smith and Gillham (1994) noted that drainage of water from the unsaturated zone occurred with decreasing IFT, thereby increasing the rate of contaminant transport from the vadose zone to the saturated zone.

It is very difficult to predict how the effects described above would compare with the spill of an ethanol gasoline containing 10% or less ethanol by volume. If mass transfer of the ethanol to the aqueous phase is rapid relative to the rate of gasoline infiltration, it is possible that some miscible displacement dynamics could dominate the overall behavior of the infiltrating gasoline. Most of the ethanol in this case could partition into the aqueous phase, causing a change in the

relative permeability of fluids in the vadose zone as the aqueous phase swells. Drainage of the ethanol-laden aqueous phase at a later time could dissolve BTEX compounds from the gasoline in a manner different than anticipated from a pool of gasohol. It is clear that changes in the retention of gasohol in the vadose zone, and the size and shape of a gasoline pool at the water table would occur due to the partitioning of ethanol into the aqueous phase and resulting reduced surface and IFTs and the reduced height of the capillary fringe. The extent of these effects is not known although this would be of particular interest in defining the overall exposure and risk potential stemming from subsurface releases of oxygenated gasolines.

2.2.2.2. Changes in Pore Structure

In addition to the impacts described above that are caused by changes in the IFT, the presence of ethanol can also change the pore structure of clay lenses, further affecting the migration of gasoline through the subsurface. Clay lenses are generally presumed to be essentially impermeable to infiltrating light nonaqueous phase liquid (LNAPL), such as gasohol. The LNAPL would typically accumulate above the clay lens, increasing the lateral extent of soil contamination in the unsaturated zone. If the spill is of sufficient volume, the LNAPL would continue to migrate vertically when the LNAPL pool reached the lateral extent of the clay lens. Changes in the pore structure that would increase the permeability of the clay lens to the gasohol would reduce the pooling of the gasohol above the lens, potentially allowing for faster infiltration to the water table and less lateral migration in the unsaturated zone. Gasohol entrapped within the clay lens represents an LNAPL source that would be difficult to remediate.

Fernandez and Quigley (1985) measured changes in the hydraulic conductivity of compacted, naturally occurring, silty clays. The hydraulic conductivity of ethanol in this soil was two orders of magnitude higher than that measured with water. Experiments with ethanol displacing pore water, followed by the introduction of a non-polar hydrocarbon, resulted in a four-order of magnitude increase in the hydraulic conductivity of the hydrocarbon. It was not clear if these changes were due to cosolvent effects or changes in the pore structure.

Stallard *et al.* (1997) studied these impacts further with ethanol and ethanol-gasoline in kaolinitic (clay) soils. Gasoline containing 10% ethanol displaced the water and entered the clay under a relatively high applied head although a standard formulation gasoline was not able to imbibe into this clay. The final permeability of the clay after the imbibition of ethanol-gasoline was 20 times greater than that of water. Magnetic resonance imaging (MRI) techniques revealed that these results occurred because of a vertical crack developed in the clay as the clay was dehydrated upon contact with ethanol. Other experiments with neat ethanol indicate that, like the results of Fernandez and Quigley (1985), ethanol displaced water at a much faster rate than water alone.

During the dehydration of clays upon contact with ethanol, some regions of the clay become more dense as the clay particles flocculate, leading to the development of other areas within the clay strata that have significantly increased porosity (Stallard *et al.*, 1997). This generation of micro- and macro-scale cracks and associated increases in permeability will greatly affect the potential for the entry of ethanol-gasoline into regions of the subsurface that a standard gasoline could not enter.

2.2.2.3. Summary of Impacts of Ethanol in the Unsaturated Zone

The material discussed above identified potential impacts of ethanol spills or ethanol-gasoline spills on the migration of the gasoline in the subsurface. None of these studies, however, is directly applicable for predicting the impacts of a spill of ethanol-gasoline at the concentrations required for California's RFG program. Direct measurement do, indeed, show that the surface tension of water with ethanol and gasoline-water IFTs drops with increasing ethanol content in the aqueous phase. The significance of these changes on the distribution of gasoline in the unsaturated zone and its spreading on the water table has not been directly studied. Based on related studies, the following processes may be of importance:

- Capillary forces

    – Reduction of the height of the capillary fringe and possible recovery of the original height could entrap gasoline droplets in the region below the water table.

    – Reduced entrapment of gasoline in the unsaturated zone.

    – Changes of unknown direction or extent in the shape and size of the gasoline pool due to reduced capillary forces around the periphery of the pool. Theoretical calculations that indicate a reduction in pool depth are inconsistent with the observed smaller pool area for the M85 versus a standard gasoline. It is possible that significant losses of methanol to the aqueous phase could have resulted in the comparison of substantially different volumes of "gasoline" in these pools.

- Effective permeabilities

    – Significant partitioning of ethanol into the aqueous phase in the unsaturated zone could affect the relative permeability of the gasoline and alter migration pathways during infiltration.

    – Dehydration and cracking of clay strata could allow ethanol-gasoline to penetrate aquitards that were previously impermeable. Mass transfer of ethanol and BTEX from cracks in a clay lens would be slower than from an unconsolidated medium.

Further study is required to understand and quantify the significance of these effects on the overall risk associated with ethanol-gasoline versus standard blend gasolines.

2.2.3. Gasoline-water Interface: Interphase Mass Transfer

2.2.3.1. Overview

Environmental releases of NAPLs, such as gasoline, contribute to the degradation of groundwater quality as the more soluble components in the organic phase are slowly leached into the aqueous phase and transported with the groundwater. With gasoline, the more highly soluble monoaromatic compounds dissolve into the aqueous phase, creating a long-term source of these hazardous constituents. This mass-transfer process is dependent on hydrodynamic conditions, chemical composition of both phases, molecular diffusion of the species, and the specific surface area between phases. The net exchange of chemical species across an interface between two phases continues until an equilibrium condition has been achieved.

The most complete study associated with mass transfer of soluble species from an alcohol-gasoline mixture was completed as a series of studies conducted for the American Petroleum Institute (API). These studies focused on the fate and transport of monoaromatic petroleum hydrocarbons from a standardized gasoline containing 85% methanol by volume (that is, M85) (Barker *et al.,* 1991; Donaldson *et al.,* 1994; Hubbard *et al.,* 1994). This M85 blend has been used to a limited extent to meet the stringent California emission requirements. Computer simulation and laboratory experiments showed that the methanol in a gasoline pool at the water table quickly dissolved into the groundwater. High aqueous-phase concentrations of benzene, toluene, ethyl benzene, and xylenes (BTEX) were also associated with the initial period of contamination because the cosolvency effect of the methanol created a slug of highly contaminated groundwater which was transported downgradient by advection. Once the methanol source was depleted from the gasoline, however, the BTEX concentrations were also reduced. While these experiments serve to help understand the possible behavior of gasoline containing ethanol, there are differences between ethanol and methanol biodegradation rates. Ethanol degrades at a rate approximately 10 times faster than methanol (Alvarez and Hunt 1999). Similar experiments with gasoline containing MTBE as an oxygenate showed negligible effects of this oxygenate on the dissolution characteristics of the BTEX compounds.

2.2.3.2. Equilibrium Partitioning

Thermodynamic equilibrium conditions for NAPL dissolution processes are often defined by Raoult's law, which enables the equilibrium aqueous-phase concentration, C_i^{*w}, to be estimated in terms of the pure liquid phase solubility, C_{s_i}, and the mole fraction, x_i^n, in the organic phase (Mackay *et al.,* 1991):

$$C_i^{*w} = C_{s_i} x_i^n \tag{2-1}$$

Raoult's law assumes that the organic phase is comprised of a mixture of similar types of organic chemicals and can, therefore, be assumed to be chemically ideal. Under ideal conditions, NAPL activity coefficients are unity, while activity coefficients for dilute concentrations of solute in the aqueous phase can usually be assumed to be constant.

Alternatively, the linear relationship can be represented with a NAPL-water partition coefficient, K^{nw}, to relate the mass concentration of a constituent in the organic phase to that in the aqueous phase:

$$K_i^{nw} = \frac{C_i^n}{C_i^{*w}} \tag{2-2}$$

Under ideal conditions, the partition coefficient is constant, making it relatively straightforward to estimate concentrations in the aqueous phase that would be in equilibrium with an organic phase.

2.2.3.2.1. Cosolvency. The polar oxygenates, such as ethanol or MTBE, are hydrophilic and can, thus, occur in high concentrations and be highly mobile in groundwater. The aqueous-phase concentration of oxygenates can, in fact, be high enough to affect the groundwater concentrations of other constituents leached from the gasoline. Of most concern are the

monoaromatic hydrocarbons, especially benzene, which is a known carcinogen. Studies of the equilibrium concentrations of gasoline constituents in water have shown that the alcohols increase solubility, and that the ethers have little effect on the solubility of carcinogenic aromatic hydrocarbons (Groves, 1988; Cline *et al.*, 1991; Poulsen *et al.,* 1992; Lojkásek and Ruzicka, 1992; Stephenson, 1992). These analyses are, however, based only on equilibrium partitioning calculations and experiments. Many processes that affect the rates of mass transfer could limit the concentrations of both the ethanol and BTEX.

The addition of oxygenates to gasoline affects the ideal equilibrium partitioning relationships by the "cosolvent effect," which is caused by the presence of high concentrations of organic compounds, such as alcohols, in the aqueous phase. These cosolvents reduce the polarity of the aqueous phase, causing a reduction in the aqueous-phase activity coefficient and allowing higher concentrations of hydrophobic organic compounds in the aqueous phase (Groves, 1988). This effect can also be explained in terms of changes in the Gibbs excess free energy associated with molecules of hydrophobic organic compounds (HOCs) in water being surrounded by cosolvent molecules as well as water molecules (Schwarzenbach *et al.,* 1993).

The significance of a cosolvent effect is dependent on the aqueous-phase solubility of the cosolvent (Pinal *et al.,* 1990). For oxygenates added to gasoline, alcohols partition preferentially to the aqueous phase, while ethers remain predominantly in the organic phase (Groves, 1988; Stephenson, 1992; Poulsen *et al.,* 1992). Thus, alcohols have a greater cosolvent effect than ethers (Cline *et al.,* 1991; Stephenson, 1992). Cline *et al.* (1991) conclude that the cosolvent effect from alcohols in gasoline will not be significant at the concentrations and residual saturations expected in subsurface systems. However, a study by Poulsen *et al.* (1992) shows that the preferential leaching of methanol during the early stages of dissolution of M85 gasoline will produce concentrations of hazardous aromatic hydrocarbons at levels that are orders of magnitude higher than without the alcohol. Rixey (1994) extended this sort of analysis to gasolines containing only 15% methanol. He concluded that significant aqueous-phase concentrations of BTEX would be present during the early stages of the dissolution process. Methanol, like ethanol, is completely miscible in water and partitions preferentially into the aqueous phase. For these reasons, its behavior as a cosolvent emulates that of ethanol.

Many of the studies that have considered the cosolvency effect of alcohols (Groves, 1988; Mihelcic, 1990; Stephenson, 1992; Peschke and Sandler, 1995; Hellinger and Sandler, 1995) utilized single HOCs as surrogates for gasoline and neglected the complexities associated with multicomponent aspects of this organic phase. Others (Letcher *et al.,* 1986; Lojkásek *et al.,* 1992) focused on the potentially detrimental hygroscopic nature of oxygenated gasolines in automobile engines. These studies provide information on the partitioning of "gasoline" but not on individual BTEX compounds. Thus, they have less utility in environmental applications.

The work by Poulson *et al.* (1992) provides much more substantial information on the partitioning of BTEX compounds from multicomponent gasolines. Methanol and MTBE were the oxygenates added to the PS-6 standard API gasoline in this work. They found that, for a given volume of gasoline, increases in the BTEX concentrations from a cosolvent effect were balanced by the reduced mass of these species in the gasoline because of the initial presence of the oxygenate. They observed significant increases in aqueous benzene concentrations only when the volume of gasoline-to-water was high.

Fernandes (1997) evaluated the effective solubilities of benzene, toluene, and xylenes (BTX) compounds in water equilibrated with a Brazilian commercial gasoline containing 22% ethanol. A range of ethanol concentrations in the aqueous phase was achieved by varying the volume ratio of water to gasoline (20:1 to 1:1) in the batch experiments. (Data collected for the Brazilian gasoline is presented in Figure 2-6.) Even with this wide range of water-to-gasoline ratios and the relatively high volume fraction of ethanol in the Brazilian gasoline, the maximum volume fraction of ethanol in the aqueous phase was on the order of 15%. These results showed that even a small concentration of ethanol in the aqueous phase (equivalent to 1%) increased the solubility of BTX compounds.

Heermann and Powers (1998) conducted an extensive study of the cosolubility effects associated with the use of ethanol in gasolines. They established BTEX and ethanol partitioning relationships by performing batch equilibrium experiments using both simple and complex "gasolines." To ensure that the entire system was well characterized, they utilized three organic solutions incorporating surrogates for the aromatic and alkane compounds comprising the majority of gasoline. They performed additional experiments with more complex commercial RFGs containing ethanol to verify results with the surrogate-compound gasolines. They measured equilibrium BTEX and ethanol concentrations in both phases, and computed the partition coefficients as a function of the aqueous-phase ethanol volume fraction.

The two commercial gasolines included a RFG containing 5.8% ethanol by volume that was obtained directly from the Phillips Chemical Company, and a generic gasoline, also containing ethanol, obtained from a local service station. The RFG obtained from Phillips Chemical Company is a certified gasoline marketed for automobile emissions testing under the California Phase II air-quality program and is here designated as the C2 gasoline. The generic gasoline was purchased from a Gas Bar station in Cornwall, Ontario, Canada. Ethanol content in that gasoline was measured to be 3.4% by volume. Additional ethanol was added to the water-gasoline mixtures to achieve a range of ethanol volume fractions in the aqueous phase.

Experimental measurements quantified the extent of BTEX partitioning from RFGs containing ethanol. The aqueous-phase concentrations displayed an approximate linear trend when they were plotted on semi-log scale at ethanol volume fractions greater than approximately 0.2 (Figure 2-7). At lower concentrations, however, there was a distinctly different trend. These differences are attributed to the hydration of the cosolvent molecules at low concentrations (Banerjee and Yalkowsky, 1988). Over the range of the maximum aqueous-phase ethanol volume fractions observed by Fernandes (equivalent to 15%), BTX concentrations in the aqueous phase that was equilibrated with the C2 gasoline generally increase by less than 50% (Table 2-2). As observed by others (Munz and Roberts, 1986), the cosolvency effect results in greater percent increases in the concentrations of the more hydrophobic xylene versus the less hydrophobic benzene. The extent of the cosolvent effect is often quantified by a cosolvency factor, which is the slope of the logarithm of the concentration versus the volume fraction of cosolvent (Banerjee and Yalokowski, 1988). The cosolvency effect measured by Fernandes (1997) and Heermann and Powers (1998) for gasohol is greater for the more hydrophobic xylene versus the less hydrophobic benzene. This trend is consistent with theory and the observations of others (e.g., Munz and Roberts, 1986).

2.2.3.2.2. Modeling Cosolubility Effects. A cosolvent present in the aqueous phase changes the partitioning of slightly soluble organic species between the organic and aqueous

phases.   Quantification of this cosolvency effect requires a more sophisticated equilibrium relationship than provided by Raoult's law (Equation [2-1]) due to the non-ideal solutions formed in the presence of the polar oxygenate. There are two general approaches to deal with these non-ideal behaviors. An empirical relationship based on experimental measurements can be used to directly estimate the distribution of an organic compound between the two phases, or a more general and rigorous thermodynamic approach can be employed to estimate activity coefficients. The use of both of these methods is complicated by the complex and unknown composition of the organic phase-commercial gasolines.   A detailed discussion of these approaches is included in Appendix A with highlights included below.

2.2.3.2.3. Empirical Cosolubility Models. The empirical models for the solubility of HOCs in non-ideal systems involve the use of both linear and log-linear equations. These equations were originally used for the solubility of pharmaceuticals but have also been applied to environmental systems (Banerjee and Yalkowsky, 1988). In general, cosolvents in water generate a logarithmic increase in HOC solubility with increasing cosolvent concentration (Pinal *et al.*, 1990):

$$log(C_i^m) = log(C_{si}^{\ w}) + \sigma_s f^c \tag{2-3}$$

where C_i^m is the equilibrium concentration of HOC i in the cosolvent mixture, $C_{si}^{\ w}$, is the solubility of HOC i in pure water, f^c is the volume fraction of the cosolvent in the aqueous phase, and σ_S is termed the *cosolvency power*.

Deviations from the log-linear cosolubility relationship (Equation [2-3]) have been observed in studies of the solubilization of non-polar drugs in a variety of cosolvent solutions (Rubino and Yalkowsky, 1987), PCBs in water-miscible alcohols (Li and Andren, 1994), and BTEX species in gasoline-methanol-water (Poulson *et al.,* 1992), and gasoline-ethanol-water (Heermann and Powers, 1998) systems. For short-chained alcohols, these deviations have been attributed to changes in the interactions between water and the cosolvent molecules (Rubino and Yalkowsky, 1987).

Because the log-linear cosolubility model (Equation [2-3]) does not incorporate the influence of interactions between the water and cosolvent molecules, this equation is only valid at higher cosolvent concentrations.   Incorporating the observed linear relation at lower cosolvent concentrations (for example, Figure 2-7), two equations can be written to reflect differences in solubilization mechanisms at low versus high cosolvent concentrations (Banerjee and Yalkowsky, 1988).

$$C_i^m = \left(1 - \frac{f}{b}\right) C_i^w + f C_i^\beta \qquad \text{for } f < \beta \tag{2-4a}$$

$$ln C_i^m = \left(1 - \frac{f - \beta}{1 - \beta}\right) ln C_i^\beta + \frac{f - \beta}{1 - \beta} ln C_i^c \qquad \text{for } f \geq \beta \tag{2-4b}$$

where β is the volume fraction of ethanol in the aqueous phase at the breakpoint between the two segments of the model, and C_i^β is the concentration of i in the cosolvent mixture at this ethanol volume fraction. These model equations are referred to as the linear/log-linear model.

2.2.3.2.4. Models for Estimating Activity Coefficients. Chemical equilibrium between two phases is defined when the chemical activity of a species is equal in the two phases. This condition provides a thermodynamic basis for estimating equilibrium concentrations based on estimates of the chemical activity of each species in the two phases. The UNIQUAC (Universal quasi chemical) model is used most frequently for multicomponent liquid-liquid equilibrium problems (Smith and van Ness, 1987). This type of model requires a significant amount of data for the system of interest. The UNIFAC (UNIQUAC functional activity coefficients) model provides the same theoretical basis as UNIQUAC although necessary binary interaction parameters are estimated from the number and type of functional groups that comprise the chemical species. Because this model does not require extensive data, it is more easily implemented than UNIQUAC although the estimation of binary interaction parameters introduces additional uncertainty in the quality of the results.

2.2.3.2.5. Application of Cosolubility Models to Alcohol-HOC Systems. Models for describing the effects of cosolvents on HOC solubilities in environmental systems have been presented by several researchers (for example, Fu and Luthy, 1986a; Groves, 1988; Pinal *et al.*, 1990). These studies generally considered the cosolvent effect where the organic phase was comprised of a single HOC. Gasoline, however, represents a highly complex mixture of organic compounds. Poulson *et al.* (1992) applied cosolvent models to describe BTEX partitioning from their experiments with PS-6 gasoline and methanol. The models appeared to provide reasonable predictions of aqueous-phase concentrations although the sparse data set available was not sufficient to adequately verify the accuracy of these models.

UNIFAC has been used fairly extensively in environmental applications. Numerous researchers have used this model to estimate the aqueous-phase solubility of HOCs in organic phase-water systems, both with and without cosolvents. Reasonable prediction capabilities in these two to three component systems—generally within a factor of two relative to experimental data—have been reported (Banerjee, 1985; Arbuckle, 1986; Fu and Luthy, 1986a; Groves, 1988; Pinal *et al.,* 1990; Mihelcic, 1990). In an effort to improve the predictive capabilities of UNIFAC for HOCs, Chen *et al.* (1993) evaluated a database of published aqueous-phase solubilities and octanol-water partition coefficients to develop a new set of binary interaction parameters better suited for environmental applications.

Kan and Tomson (1996) recently completed a comprehensive evaluation of the applicability of UNIFAC for predicting aqueous solubilities of environmentally significant HOCs. With several different sets of published values of the vapor-liquid functional group binary interaction parameters, they found excellent agreement between experimentally measured and predicted solubilities of pure chemicals in water. In general, the predictions were within one order of magnitude of the measured solubilities with the greatest discrepancies observed for high molecular weight or chlorinated hydrocarbons. However, as with most other applications, the analysis of Kan and Tomson (1996) involved systems with only two to three components.

Hellinger and Sandler (1995) examined the quality of both UNIQUAC and UNIFAC to model their measured gasoline-water-oxygenate solubility data. In both experimental and modeling aspects of their work, they considered single alkane species as surrogates for all

species in the gasoline and *t*-amyl methyl ether or *t*-amyl alcohol as the added oxygenates. Both UNIFAC and UNIQUAC provided qualitative descriptions of trends in the ternary diagrams representing equilibrium compositions of the two phases. However, neither was accurate in a quantitative sense, especially for the solubility of the alkane in the aqueous phase.

Three mathematical models were applied to the experimental results obtained by Heermann and Powers (1998). These models were applied in a true predictive manner based on the volumes of gasoline and water equilibrated and the initial concentration in the gasoline. Figure 2-8 shows representative results of these predictions. The log-linear and UNIFAC models were capable of representing the overall increase in concentration as a function of increasing ethanol content in the aqueous phase. However, neither of them mimicked the observed two-part curve. A piecewise model comprised of a linear relationship for low ethanol volume fractions and a log-linear model for higher concentrations was fit to data for a surrogate gasoline comprised of seven compounds. These parameters were then used to predict BTEX concentrations in the aqueous phase equilibrated with commercial gasolines. This model was superior to the UNIFAC predictions, especially at the low ethanol concentrations expected when gasolines presently sold are spilled in the environment. Thus, the linear/log-linear model presented by Heermann and Powers (1998) can be utilized to best predict groundwater contamination by gasolines containing ethanol when the relative volumes of the two phases and the gasoline composition can be estimated.

2.2.3.3. Rate-limited Interfacial Mass Transfer

2.2.3.3.1. General Concepts. The interphase mass transfer of ethanol and hydrocarbons between gasoline and groundwater can be most simply expressed as a product of a mass-transfer coefficient and a concentration difference (Cussler, 1984)

$$N_i = k_i \left[\frac{C_i^n}{K_i^{n,w}} - C_i^w \right] \tag{2-5}$$

where N_i is the flux of compound i; k_i is the mass-transfer coefficient; C_i^w and C_i^n are the concentrations of compound i in phases *a* and *b*, respectively; and $K_{i,}^{n,w}$ is a partition coefficient describing the equilibrium partitioning relationship of the compound between the two phases (Equation [2-5]).

The mass-transfer coefficient, k_i, reflects rate limitations to interphase mass transfer resulting from the noninstantaneous transport of compounds to and away from the phase boundary. Thus, for a gasoline pool, ethanol and hydrocarbons must be transported through the gasoline to the phase boundary separating the gasoline and groundwater and must be transported away from the boundary with the groundwater. Appendix B provides additional details addressing the mass-transfer rate coefficient.

In most interphase mass-transfer models, the boundary is conceptualized as a two-dimensional surface with no thickness. Therefore, mass cannot accumulate at the boundary; and the physical constraint exists that the rate of transport to the boundary equals the rate of transport away from the boundary (Taylor and Krishna, 1993). Because of the sequential nature of the mass transfer and the constraints on the transport rates, a single transport process will often

govern the overall interphase mass-transfer rate. That process, which typically exhibits the slowest rate of transport, is, thus, rate limiting.

The rate at which ethanol is transported from gasoline to groundwater will largely determine the magnitude and the duration of the cosolvency effect. Very rapid rates of ethanol mass transfer would lead to greater ethanol concentrations in groundwater that would further lead to increased hydrocarbon concentrations because of cosolvency. The rate of mass transfer would govern the duration of the cosolvency effect as a result of a more rapid depletion of ethanol.

Transport processes differ greatly between gasoline and groundwater. For example, a gasoline-phase pool is held largely motionless by capillary forces while the groundwater moves beneath it at a relatively steady rate. Some of the most important transport processes are described below, first for the gasoline, and then for the groundwater.

2.2.3.3.2. Rate Limitations in the Gasoline Phase. The vast majority of both analytical and numerical mathematical models of mass transfer from NAPL pools assume that the interphase mass transfer of HOCs is limited by the rate of groundwater transport away from the NAPL-groundwater boundary. Inherent in these models is the assumptions that the composition of the NAPL phase is homogeneous and remains constant over time. For standard formulation gasolines, these assumptions may be reasonable because the gasoline composition changes very gradually as a result of low solubilities and dissolution rates.

The presence of ethanol in gasoline, however, will likely invalidate the above assumptions. Because ethanol partitions preferentially into water, it may be nearly depleted from the gasoline at the boundary.   For very slow rates of ethanol transport to the boundary, an ethanol concentration gradient develops through the gasoline, invalidating the assumption that the chemical composition is homogeneous over the depth of the pool. For a sufficiently slow ethanol transport, the net interphase mass-transfer rate will approximately equal the rate of ethanol transport through the gasoline. In contrast, for very rapid rates of ethanol transport, concentration gradients will be small, but the ethanol will be rapidly depleted from the gasoline invalidating the assumption that concentrations do not vary over time. For sufficiently fast ethanol transport through the gasoline, transport via groundwater will define the mass-transfer, rate-limiting process.

Two transport processes—molecular diffusion and free convection—have been identified that contribute to the transport of ethanol and other hydrocarbons through the gasoline. Molecular diffusion, which describes the net movement that occurs when molecules undergoing random motion are subjected to a concentration gradient, is a generally well understood process and is fairly easily modeled (for example, Cussler, 1984; and Taylor and Krishna, 1993). Free convection refers to the process where bulk-fluid flow occurs as a result of an unstable condition created when the fluid density increases vertically upwards. It has only recently been studied with respect to gasoline (Heermann and Powers, in preparation) and is a much more difficult process to model.

2.2.3.3.3. Molecular Diffusion. Molecular diffusion in a subsurface gasoline pool can be described mathematically by Fick's law:

$$J_i = -\frac{D_i}{t}\frac{C_i}{z} \tag{2-6}$$

where J_i is the diffusion flux of compound i, D_i is the diffusion coefficient,   is the tortuosity, C_i is the concentration, and z is the vertical dimension. For simplicity, diffusion in Equation (2-6) is considered to occur only in the vertical (z) direction within the gasoline pool but may be generalized to include diffusive transport in all directions.

Holman and Javandel (1996) utilized the assumption that molecular diffusion of ethanol and hydrocarbons through a NAPL is the primary rate-limiting process governing interphase mass transfer to a groundwater body. They published a semi-analytical solution for time-dependent transport in an aquifer from an LNAPL pool with interphase mass transfer being controlled by diffusive transport in the LNAPL. Molecular diffusion in gasoline to a groundwater boundary could also be modeled using multicomponent multiphase numerical models. One model, MOFAT (Katyal *et al.,* 1991), is in the public domain, but numerous other such computer models exist in universities or can be acquired commercially. Both the semi-analytical and numerical models consider depletion of the compound from the gasoline as well as concentration gradients that develop in the gasoline due to the removal of ethanol and other gasoline hydrocarbons at the groundwater boundary

2.2.3.3.4. Free Convection. Free convection occurs when a density gradient exists within a single fluid. If the gradient is such that the fluid is less dense near the bottom, a physically unstable fluid profile is created. As a result, a convective flow is established within the fluid, typically as "fingers," thereby blending the high- and low-density portions of the fluid. Figure 2-9 illustrates this concept.

Most gasoline has a density less than that of ethanol because the alkanes, cycloalkanes, and alkenes comprising the majority of most gasolines have densities less than the density of ethanol (ρ_{etoh}=0.789 g/mL). Therefore, gasoline with ethanol generally has a greater density than gasoline without ethanol.   For example, the Phillips Chemical Company C2 gasoline contains 5.8% ethanol by volume and has a specific gravity of 0.741 at 20°C. When the ethanol is removed from the C2 gasoline, its density falls to 0.738 g/mL.

In the subsurface, as the ethanol is removed from the gasoline at the gasoline-groundwater interface, the density of the gasoline at the boundary becomes less than its density in the region above the boundary. As a result, the high- and low-density gasoline regions become unstable with respect to each other; and, consequently, the gasoline with the higher ethanol content and greater density flows downwards to the phase boundary while the less dense, ethanol-depleted gasoline moves upwards. In a series of column experiments, Heermann and Powers (in preparation) found that free-convective flow greatly increased the rate of ethanol transport to the boundary relative to diffusional transport.

The higher rate of interphase mass transfer resulting from free convection will likely lead to greater ethanol concentrations in groundwater and, therefore, to a greater cosolvency effect. However, the higher mass-transfer rate will yield a more rapid depletion of the ethanol in the gasoline.

Because all of the BTEX compounds have densities greater than ethanol, a gasoline with very high fractions of BTEX compounds could have a density greater than ethanol. Heermann and Powers (in preparation) demonstrated that, when the density of the bulk gasoline exceeds that of ethanol, the ethanol is transported primarily by the much slower molecular-diffusion mechanism.

2.2.3.3.5. Rate Limitations in the Groundwater. The net rate of transferring ethanol and hydrocarbon species from the gasoline to the groundwater may also be limited by mechanisms controlling the transport of these species via groundwater away from the gasoline-water interface. Mass transport in groundwater is largely controlled by the processes of advection and hydrodynamic dispersion. Advection is the principal means of transporting hydrocarbons horizontally away from the gasoline-pool boundary with the flowing groundwater while hydrodynamic dispersion is the principal means for vertical transport away from the gasoline pool. The net rate of interphase mass transfer increases with increased groundwater flow rates and dispersion because these processes reduce the concentration of solute near the interface.

2.2.3.3.6. Net Rate Limitations. Molecular diffusion in gasoline is generally a very slow transport process in comparison to the groundwater transport processes of advection and dispersion. Thus, if diffusion were the only transport process in the gasoline, it would likely be the rate-limiting step under most subsurface conditions.

Free convection is apparently a much more rapid transport process that exists, in theory, for all ethanol-bearing gasolines except those with very high aromatic fractions. With the higher rates of mass transfer associated with free convection, the concentrations of both ethanol and BTEX species in the groundwater are expected to be higher in comparison with those resulting solely from diffusion. The ethanol, however, will be depleted from the gasoline source more rapidly when free convection is the dominant process, reducing the period of time that the ethanol influences BTEX dissolution rates. Following the depletion of ethanol from the gasoline, the remaining pool of gasoline would behave as a standard blend gasoline. However, there is insufficient knowledge about free convection in subsurface gasoline lenses to determine whether this process would likely define the rate-limiting process or whether it is sufficiently fast such that advective/dispersive transport via groundwater would become the rate-limiting process.

2.2.4. Transport with the Aqueous Phase

2.2.4.1. Modeling Groundwater Transport

The transport of dissolved hydrocarbons in the groundwater via advection and hydrodynamic dispersion may be modeled using one or more of the numerous solutions available for the advection-dispersion equation. The advection-dispersion equation is a generalized differential equation describing the advective and dispersive transport and the addition and removal of dissolved compounds in groundwater.

The primary source of ethanol and gasoline hydrocarbons is the overlying gasoline pool. These compounds enter the groundwater domain via the interphase mass-transfer mechanisms discussed above. Examples of analytical models developed for the transport from NAPL sources by groundwater include those of Hunt *et al.* (1988); Johnson and Pankow (1992); Voudrias and Yeh (1994); Holman and Javandel (1996); Chrysikopoulos and Lee (1997); and Chan and Javandel (1998). All of these except for Holman and Javandel (1996) and Chrysikopoulos and Lee (1997) assume that the chemical composition of the NAPL source is homogeneous throughout the depth of the pool and remains invariant with time. The analytical solution of Chrysikopoulos and Lee (1997) permits the composition of the NAPL pool to vary over time; and, as discussed above, the solution of Holman and Javandel (1996) permits the composition of the NAPL to vary spatially and temporally. Potential sources of hydrocarbons in the

groundwater are the organic-phase blobs that may form below the gasoline pool as a result of water-table fluctuations or due to phase separation that may occur when ethanol concentrations are reduced (Section 2.2.4.3).

Two critical hydrocarbon-removal processes include the adsorption of the hydrocarbons to sand, clay, or other solid materials in the subsurface, and the biologically mediated chemical transformation of the ethanol and hydrocarbons. Adsorption is reversible to varying degrees so that when concentrations of dissolved hydrocarbons decrease, the adsorbed hydrocarbons may be released back into the aqueous phase. Biologically mediated chemical transformations are generally not reversible and, thus, serve only as a removal mechanism for hydrocarbons. However, because these processes generate new compounds, biochemical transformations may act as sources and/or sinks for compounds other than BTEX.

The presence of ethanol in groundwater may potentially alter the processes of adsorption and biodegradation. It may reduce the adsorption of other petroleum hydrocarbons due to reductions in the aqueous-phase chemical activities of those hydrocarbons. Ethanol may also affect biodegradation. A discussion of the role of ethanol on subsurface biodegradation is presented by Alvarez and Hunt (1999).

2.2.4.2. Adsorption with Reduced Chemical Activities

Adsorption may be described by a number of "isotherms," or mathematical relations between the concentration of a compound dissolved in water and its equilibrium concentration sorbed to a solid. One widely used isotherm is the Freundlich isotherm (Fu and Luthy, 1986b) which relates the equilibrium aqueous-phase concentration of compound i, C_i^w, and the concentration of i sorbed to the solid phase:

$$S_i = K_p C_i^{w^n} \tag{2-7}$$

The partition coefficient, K_p, which describes equilibrium partitioning between the aqueous phase and the surface of the solid material, and the exponent n are empirical fitting parameters. In environmental analyses, S_i, is generally expressed in units of mass per unit-mass of soil; so K_p correspondingly has units of volume per unit-mass.

When a cosolvent is present in the aqueous phase, the partition coefficient, K_p, decreases. This has been documented by a number of researchers, including Rao *et al.* (1985), Nkedi-Kizza *et al.* (1985), Fu and Luthy (1986b), Rao *et al.* (1990), Kimble and Chin (1994), Barrett *et al.* (1994), and Errett *et al.* (1996). Nkedi-Kizza *et al.* (1985) demonstrated that log-linear cosolvency relationships similar to Equation (2-3) could be applied to adsorption and showed that K_p decreased in an approximate logarithmic manner with increasing volume fraction of cosolvent in the aqueous phase:

$$log \frac{K_{p_i}^m}{K_{p_i}^w} = -\alpha\sigma_s f^c \tag{2-8}$$

In Equation (2-8), K_{pi}^m and K_{pi}^w are the adsorption partition coefficients for compound i with the superscripts indicating equilibrium with a water-cosolvent mixture (*m*) and with pure water

(*w*). Rao *et al.* (1985) and Fu and Luthy (1986b) provided theoretical explanations for the observed behavior analogous to those developed for the liquid aqueous-organic phase partitioning in the presence of a cosolvent. Using methanol as a cosolvent, Fu and Luthy (1986b) showed that the adsorption partition coefficient decreased in a log-linear manner, much the same as the solubility increases with cosolvent fraction. They compared the effects of cosolvency on adsorption and solubility and found that the slope of the log-linear plot for adsorption was about half that for solubility. Letting the cosolvency factor σ_s be equal for the solubility and adsorption partition coefficient, then α in Equation (2-8) would have a magnitude of about 0.5. The authors explained the difference was from the swelling of the organic carbon associated with the soil to which the HOCs sorb. Brusseau *et al.* (1990) showed that the log-linear model could be extended to include the kinetic parameters describing desorption rates.

As an alternative to the empirical log-linear approach, one may estimate the effect of ethanol on the partition coefficient, using aqueous-phase activity coefficients. This was demonstrated earlier for computing liquid-phase partitioning with the activity coefficients computed, using a thermodynamic model, such as UNIFAC or UNIQUAC (see a more thorough description in Appendix A). Assuming that the ethanol effects only the aqueous-phase hydrocarbon activities and has no effect on the solid surfaces upon which adsorption takes place, then one may simply scale the adsorption partition coefficient:

$$K_{p_i}^{w,c} = \frac{\gamma_{p_i}^{w,c}}{\gamma_{p_i}^{w}} K_{p_i}^{w} \tag{2-9}$$

where $\gamma_{p,i}^{w,c}$ is the activity coefficient of compound *i* in a water-cosolvent solution, and $\gamma_{p,i}^{w}$ is the activity coefficient of compound *i* in pure water (Rixey, 1994).

One of the chief effects of adsorption is the retardation of hydrocarbons in such way that their effective velocities become less than the groundwater that is transporting them. In a one-dimensional modeling study to compare BTEX concentrations downgradient of an M85 gasoline release, Rixey (1994) showed that when cosolvent dependent adsorption was incorporated into the model, the BTEX compounds moved more rapidly through the porous medium. The methanol and BTEX were assumed to be added instantaneously to the aqueous phase, and so the downgradient concentrations appeared as discrete peaks. The effect was more pronounced for benzene than the other BTEX compounds because benzene is the least hydrophobic of the BTEX compounds and so moved through the porous medium with nearly the same velocity as the methanol and water. Because toluene did not move synchronously with the methanol, the cosolvency effect of the methanol was less than for benzene. Rixey (1994) also found that cosolvency effects were only significant where downgradient aqueous methanol concentrations exceed 10–13 wt%.

2.2.4.3. Phase Separation Due to Dilution of Ethanol Concentrations

In the aqueous phase, because ethanol and gasoline hydrocarbons mix with uncontaminated groundwater and biodegrade, ethanol and gasoline hydrocarbons concentrations will generally decrease with increasing distance from the NAPL source. As a result of the approximate log-linear relation between aqueous HOC solubility and ethanol concentration, the aqueous phase

may become supersaturated with respect to the hydrocarbons, resulting in the formation of a liquid organic phase. The general concept of phase equilibrium and phase separation was addressed in Section 2.1 for ethanol-bearing gasolines.

Rixey and Dortch (1992) and Donaldson *et al.* (1994) investigated the phenomenon of phase separation for alcohol gasolines, using a pulse injection of gasoline comprised of 85% methanol (M85). Given a release of M85 gasoline into the subsurface, the gasoline would initially be completely miscible with water; and a NAPL would not form. However, as the fraction of water in that initial mixture increases due to dispersion and biodegradation, the ethanol fraction decreases, and the gasoline becomes immiscible with water. Donaldson *et al.* (1994) observed the process leading to the formation of a separate phase, primarily via column and pore-scale visualization models. The pore-scale visualization studies of Donaldson *et al.* (1994) revealed the formation of NAPL droplets on sand grains. These droplets became entrapped in the pore structure and consequently reduced the permeability of the porous medium to water. Rixey and Dortch (1992) also observed the formation of a separate NAPL phase when the methanol content dropped to below 77%. They used a numerical modeling approach to estimate the distribution of residual organic NAPL that precipitated as a result of a decrease in methanol concentrations.

If the composition of the aqueous phase becomes undersaturated with respect to the hydrocarbon concentrations (that is, if the chemical activities in the NAPL are greater than in the aqueous phase), the residual phase may re-dissolve into the groundwater. Thus, the precipitated gasoline droplets will act as a latent source of hydrocarbons. If the residual phase exists as well-dispersed droplets below the gasoline pool, then their higher surface areas will increase the rate of mass transfer, ultimately resulting in higher aqueous-phase hydrocarbon concentrations. The dissolution of entrapped NAPL has been investigated extensively by others (for example, Hunt *et al.,* 1988; Powers *et al.,* 1992, 1994; Geller, 1990).

The phase-separation studies discussed above considered only M85 gasolines that are initially miscible with water. It has not been determined whether hydrocarbons that solubilize in groundwater from a lens of gasoline containing much smaller quantities of ethanol are likely to form a separate organic phase as the ethanol concentration decreases.

2.2.5. Special Considerations

2.2.5.1. *Neat Ethanol Dissolving Prior Contaminants*

Because of ethanol's hygroscopic nature, ethanol and gasoline are transported and stored separately until the final stages of the distribution process (Section 2.1). The potential, therefore, exists for neat ethanol to be released into the subsurface primarily from storage tanks or shipping containers. Where NAPLs already exist in the subsurface, the release of pure ethanol may influence the subsurface distribution of these NAPLs and enhance the transport of its constituents via groundwater.

The influence of neat ethanol on subsurface processes is expected to be nearly identical to those of gasohol except that its influence may be magnified. Two differences are important:

- The quantities and concentrations of ethanol will be greater; and

- The elimination of rate-limiting interphase mass transfer of ethanol from the gasoline to vadose-zone water or groundwater.

Increases in the aqueous phase solubilities would affect both BTEX and MTBE species that were initially present in the gasoline pool. The potential increase would depend mostly on the ethanol concentration in the aqueous phase. As described in Section 2.2.3.2, BTEX concentrations could increase by a few orders of magnitude right at the spill zone. There have been no studies conducted to predict increases in MTBE concentrations. Cosolvency effects depend greatly on the hydrophobicity of the organic species. Because MTBE is much more hydrophilic than BTEX, the cosolvency effect will be much less. This means that the percent increase in the aqueous phase concentrations of MTBE will not be as great as for BTEX species.

Based upon the understanding of the influence of ethanol on subsurface flow and transport processes (Sections 2.1–2.4), releases of neat ethanol are expected to (1) increase the aqueous solubility and, hence, the dissolution rates of NAPL compounds; (2) reduce the mass of organic compounds sorbed to the solid phase; and (3) reduce the IFT between NAPL and the aqueous phase and, thereby, potentially enable the NAPL to migrate.

Increased solubility and decreased adsorption were the subject of a laboratory investigation by Chen and Delfino (1997), who studied the effects of fuels containing 85% ethanol or methanol on HOC solubility. Solubilities and adsorption partition coefficients of 18 polynuclear aromatic hydrocarbons (PAHs) were determined for a soil contaminated with coal tar. The study demonstrated that the PAH solubilities increased in an approximate log-linear manner with increasing fractions of ethanol (Equation [2-3]), while the adsorption partition coefficients decreased in an approximate log-linear manner (Equation [2-8]).

The effects of high concentrations of ethanol on NAPL dissolution were investigated in two field studies that focused on the use of ethanol as a method to accelerate the removal of NAPLs during subsurface remediation. In one study, researchers injected 40,000 L (11,000 gal) of a solution comprised of 70% ethanol, 12% *n*-pentanol, and 18% water into the subsurface to determine the extent to which the alcohol solution would dissolve entrapped NAPL, consisting of jet fuel and chlorinated solvents (Rao *et al*., 1997). The alcohol solution and the dissolved NAPL constituents were recovered in downgradient wells. The researchers found that, on average, 90% of NAPL constituents were removed following the injection and recovery of the alcohol. This study clearly demonstrated the importance of the cosolvency effect at high ethanol concentrations.

In another field study by de Oliviera (1997), ethanol was injected into a sand aquifer containing gasoline at residual saturation. The study was performed in order to observe the dynamics of ethanol flushing and to assess the effectiveness of ethanol flushing as a means of enhancing the removal of gasoline from the subsurface. As with the previous study, ethanol was injected below the water table via a well; and the ethanol and gasoline were recovered via a downgradient well. In this study, the ethanol migrated upwards and, thus, failed to uniformly remove the residual gasoline.

The studies cited above focused upon solubility and adsorption changes resulting from ethanol. Currently, a knowledge gap exists regarding the effects of high ethanol concentrations in the vadose zone, especially those pertaining to changes in IFT. Based on existing understanding outlined in Sections 2.2, it is expected that, as ethanol migrates downward through the vadose zone, it will dissolve primarily in the aqueous phase. The resulting reduction in the water-air and water-NAPL IFT is expected to alter moisture profiles and may mobilize residual

gasoline entrapped in pores. Because of the highly preferential partitioning of ethanol into water, ethanol is not expected to dissolve in the NAPL pool.

As neat ethanol or ethanol-water mixtures migrate to the water table, the ethanol-rich solution may be entrapped within the capillary fringe. A laboratory and computer modeling study by Jawitz *et al.* (1998) looked at the displacement of water by a solution of 70% ethanol in water along a two-dimensional, cross-sectional pathway. The researchers found that the ethanol-rich solution migrated towards and became entrapped within the capillary fringe immediately above the water table because of buoyancy forces. The ethanol dissolved into the groundwater but at a rate limited by the mass transfer of ethanol away from the capillary fringe.

2.2.5.2. Oxydiesel

Oxydiesel is comprised of chemical constituents different than those comprising gasohol. Diesel and oxydiesel fuels contain much smaller quantities of the least hydrophobic BTEX compounds contained in gasoline and gasohol and instead contain greater quantities of compounds of higher molecular weight that are generally less water soluble than those in gasoline.   Because the cosolvency effect generally increases with decreasing solubility (Appendix A), increases in the solubilities of oxydiesel constituents are expected to be greater on average than those in gasohol. However, the solubilities of diesel constituents increase from low baseline solubilities values relative to the BTEX compounds in gasoline; and despite higher cosolvency factors, the increased solubilities of the oxydiesel compounds would likely remain relatively low.

2.2.6. Examples of Modeling Efforts

Although there are numerous uncertainties in the specific mechanisms affecting the migration and dissolution of ethanol gasolines and the subsequent transport of ethanol and BTEX species with groundwater, a few studies have been completed to predict the effect of the ethanol on the net transport of soluble species. The study by Malcolm Pirnie, Inc. (1998) which is described below, includes a two-dimensional modeling effort to predict the transport of ethanol and benzene. Biodegradation and retardation were included in this effort, but the dissolution source term was unknown. On the other hand, Heermann and Powers (1996) had a more rigorous approach for describing the dissolution rate term, but they neglected biodegradation in the aquifer.

2.2.6.1. Effect of Biodegradation

The Malcolm Pirnie, Inc. (1998) modeling effort was aimed at quantifying changes in the length of a contaminant plume due to the addition of ethanol to gasoline. The researchers employed an analytical solution to the two-dimensional transport equation for these predictions. This approach included advection (1-D), dispersion (2-D), retardation, biodegradation, and a constant concentration of ethanol and benzene at the gasoline pool. The following assumptions were used in this analysis:

- Benzene does not biodegrade when the ethanol concentrations are greater than 3 mg/L. Below this threshold value, it degrades following a first-order rate law ($=0.0062$ day^{-1}).

- Ethanol also degrades according to a first-order rate law ($=0.014 \ \mathrm{day}^{-1}$). The approach used to determine this constant was justified well.

- Adsorption of benzene can be described with a standard retardation approach; ethanol does not sorb.

The ethanol and benzene concentrations at the gasoline source are constant over time. It was assumed that ethanol concentrations near the source are 4000 mg/L, which is based on an ethanol concentration of 5% by volume in gasoline with a tenfold-dilution factor. Benzene was assumed to enter the water table at a concentration of 8 mg/L, a concentration which is representative of typical leaking underground storage tank (LUST) sites.

The aqueous-phase velocity (v = 0.004–0.4 ft/d) and fraction of organic carbon in the soil matrix (f_{oc}=0.005–0.01) were used as variables in this analysis.

As expected, based on the assumptions regarding the nature of the benzene biodegradation rates, the benzene plume traveled further when ethanol was present. With the variable velocity and retardation values, the benzene plumes were predicted to extend 17–34% further than in the absence of ethanol. For example, at v=0.4 ft/d and f_{oc}=0.005, the benzene plume traveled 220 ft without the ethanol present versus 280 ft in the presence of ethanol. Figure 2-10 illustrates the general nature of the simulation results.

This first-order analysis does provide some insight into the nature of this problem. However, no sensitivity analysis was performed relative to the high degree of uncertainty in degradation rate constants for ethanol and benzene and the critical ethanol concentration above which benzene is not degraded. Presently, ethanol biodegradation rate constants are only available for laboratory-scale microcosms (Corseuil *et al.*, 1998) at 28°C. In the Malcolm Pirnie, Inc. (1998) analysis, laboratory-measured rates on the order $= 0.1$ to $0.5 \ \mathrm{d}^{-1}$ were extrapolated to field conditions to account for lower concentration of microorganisms and colder temperatures (15°C). Although the methods employed for this extrapolation were based on sound scientific basis, considerable uncertainties exist in the estimated ethanol decay rate ($= 0.014 \ \mathrm{d}^{-1}$). With the very conservative rate of decay of ethanol in the subsurface, the distance traveled by ethanol would be overestimated; and, thus, the percentage increase in the travel distance of the benzene plume would also be overestimated.

Based on the analysis of Heermann and Powers (1996) (Section 2.2.6.2 below), the estimated concentrations of ethanol and benzene appear to be reasonable. However, the Malcolm-Pirnie, Inc. (1998) analysis did not account for eventual depletion of ethanol from the source. Once ethanol is depleted from the source, natural attenuation of the BTEX would return to the levels expected from a spill of a standard gasoline. Thus, based on the assumptions regarding dissolution, the Malcolm Pirnie, Inc. (1998) estimates could be an overestimate of the impact of the ethanol on benzene plume lengths.

The combined conservative estimates of the ethanol biodegradation rate and lack of inclusion of the depletion of ethanol from the gasohol source suggest that the Malcolm Pirnie, Inc. (1998) analysis represents a worst case scenario. Significant uncertainties in the biodegradation rate constants and concentrations of ethanol and benzene at the gasohol source prevent improved quantitative assessments of the overall impact of ethanol on the length of a benzene plume.

2.2.6.2. Effect of Cosolvency

Heermann and Powers (1996) investigated increases in the transport of BTEX species resulting purely from cosolvency.   For this study, the U.S. Geological Survey's cross-sectional, flow- and solute-transport model, MOCDENSE (Sanford and Konikow, 1985), was modified to create a source term that simulated the interphase mass transfer of ethanol and a BTEX compound from a gasoline into groundwater.

The study considered an aquifer with a saturated thickness of 5 m (16.5 ft), as illustrated on Figure 2-11. Groundwater in the aquifer flowed with a uniform velocity of 0.1 m per day (0.33 ft per day). The horizontal and transverse dispersivities were 1 m (3.3 ft) and 0.1 m (0.33 ft), respectively, and the effective porosity of the aquifer was 0.25.

A gasoline pool at the water table, 10 m in length by 0.5 m thick, was comprised of three surrogate compounds that included *iso*-octane, m-xylene, and ethanol. *Iso*-octane represented the composite physiochemical properties of the alkane, alkene, and cycloalkane hydrocarbons while *m*-xylene served as a surrogate for the monoaromatic (BTEX) compounds in gasoline. To assess the impact of the ethanol on the transport of *m*-xylene, model simulations were performed considering both ethanol-bearing and ethanol-free gasolines. The ethanol-bearing gasoline was comprised of 10% ethanol by volume, 13.5% *m*-xylene, and 76.5% *iso*-octane; the ethanol-free gasoline was comprised of 15% *m*-xylene and 85% *iso*-octane.

Ethanol and *m*-xylene source rates were computed at each gasoline boundary cell using Equation (2-5). Ten boundary cells were used to add ethanol and *m*-xylene to the groundwater domain. Each boundary cell was 1 m in length and 0.1 m deep. In the gasoline domain, the *iso*-octane, *m*-xylene, and ethanol concentrations were allowed to vary over time in the gasoline. However, the gasoline was assumed to be well mixed vertically.

To address uncertainties pertaining to mass-transport processes in the gasoline and their representation using Equation (2-5), the mass-transfer coefficient was varied from 10^{-8} to 10^{-3} meters per second (m/s). The latter value was sufficiently high to maintain chemical equilibrium between the gasoline and groundwater phases at the boundary. The partition coefficient was estimated using log-linear models for *m*-xylene and ethanol with parameters determined by fitting the models to laboratory data.

Contours of simulated aqueous-phase ethanol and *m*-xylene concentrations are shown on Figure 2-12 for the elapsed period of 180 days. For the case of equilibrium between the gasoline and the groundwater table ($k_i=10^{-3}$ m/s), the modeling analyses showed an approximate 10% increase in the distance to the leading edge of the *m*-xylene plume at 180 days due to the presence of ethanol in the gasoline.   However, when smaller interphase mass-transfer coefficients were used, the size and extent of the *m*-xylene was essentially unaffected by the presence of ethanol. Ethanol was more than 90% depleted from the gasoline within several days under the local equilibrium assumption ($k_i =10^{-3}$ m/s) and was more than 99% depleted in less than 90 days. In contrast, ethanol was only about 10% depleted from the gasoline at 180 days for $k_i = 10^{-8}$ m/s.

The above study demonstrates that the presence of ethanol in gasoline can produce a small but finite increase in the mass transfer of BTEX compounds from gasoline to groundwater and an increase in the size of a BTEX plume. Whether the impact is negligible or measurable depends upon transport mechanisms in the gasoline. Free convection may provide a sufficiently

fast transport mechanism (Heermann and Powers, in preparation) to permit local chemical equilibrium between the gasoline and groundwater.

The Heermann and Powers (1996) study only provides an estimate of the increase in plume length via cosolvency mechanisms. The processes of adsorption and biodegradation would result in a decreased plume size, although this reduction would less in the presence of ethanol than for a standard gasoline. The influence of cosolvency on adsorption is dependent on the composition of the aquifer material. Adsorption will be greater for aquifer material with a high fraction of natural organic material (NOM); and so cosolvency will decrease the extent of adsorption and, thereby, enhance the length of BTEX plumes to a greater degree for systems with higher quantities of NOM.

The study did not explicitly determine the influence of the gasoline-pool size on the length of the BTEX plume. However, it could be deduced that for the case of local equilibrium between the gasoline pool and the groundwater at the phase boundary, that a thicker gasoline pool will result in a much greater concentrations of ethanol in the groundwater due to the greater mass of ethanol. Higher ethanol concentrations would produce a much greater cosolvency effect and the length of the BTEX plume would be more greatly enhanced. Any deduction regarding the effect of the lateral extent of the gasoline pool on the BTEX plume would be speculative. A much more thorough modeling study and sensitivity analysis would be required to further evaluate the range of impacts that the ethanol and cosolvency effect would have on the extent of the BTEX plumes.

2.3. Acknowledgements

2.4. References

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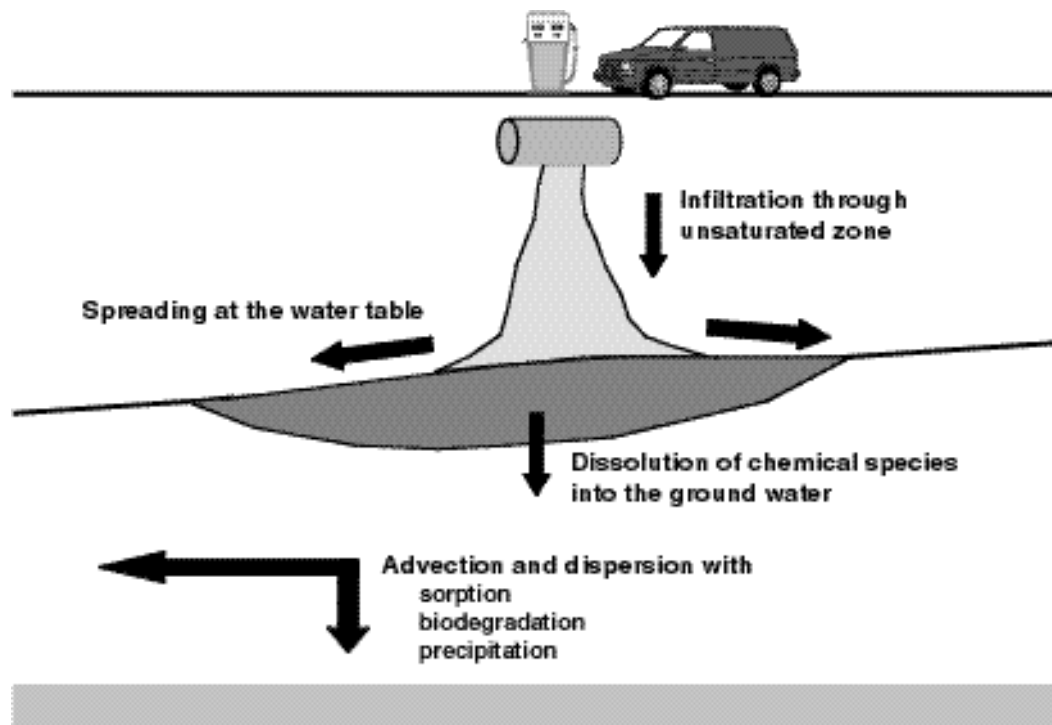
Figures

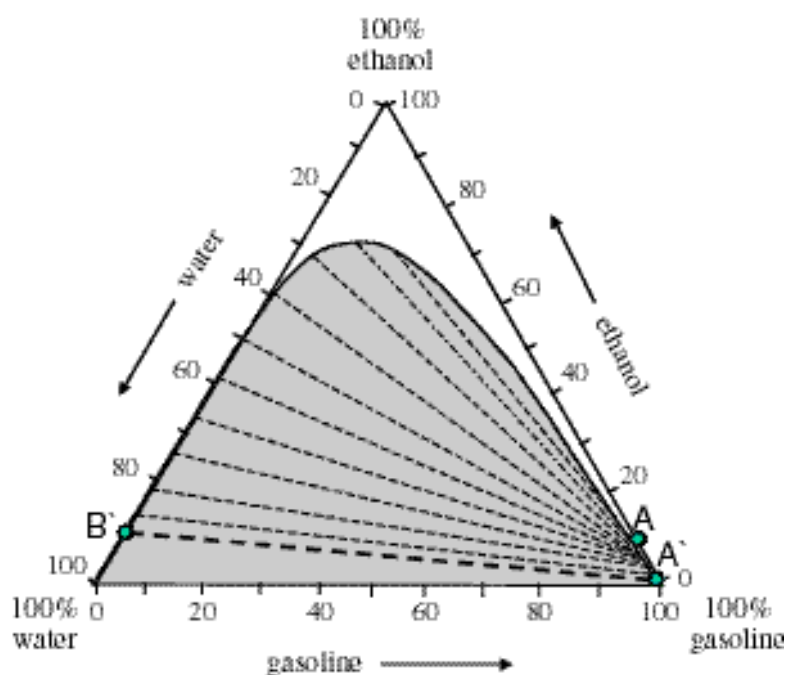**Figure 2-1. General processes governing the fate of gasolines in the subsurface.**

Figure 2-2. Ternary-phase diagram for gasoline-ethanol-water system at 21°C. The shaded region represents the region where the total mass fractions separate into two phases. The ends of the dashed (tie) lines indicate the composition of each phase at equilibrium. Axes represent mass percentages (adapted from de Oliveira, 1997).
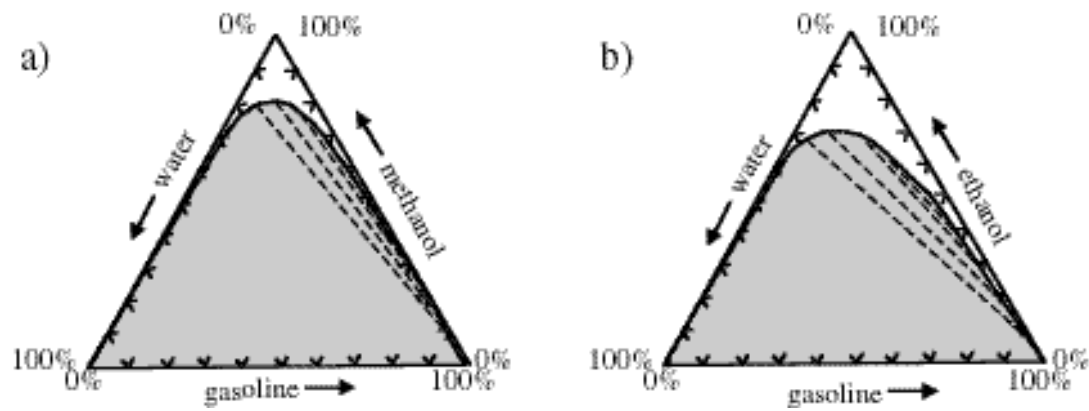
Figure 2-3. (a) Ternary-phase diagram for gasoline-methanol-water system and (b) gasoline-ethanol-water system (adapted from Letcher *et al.*, 1986).
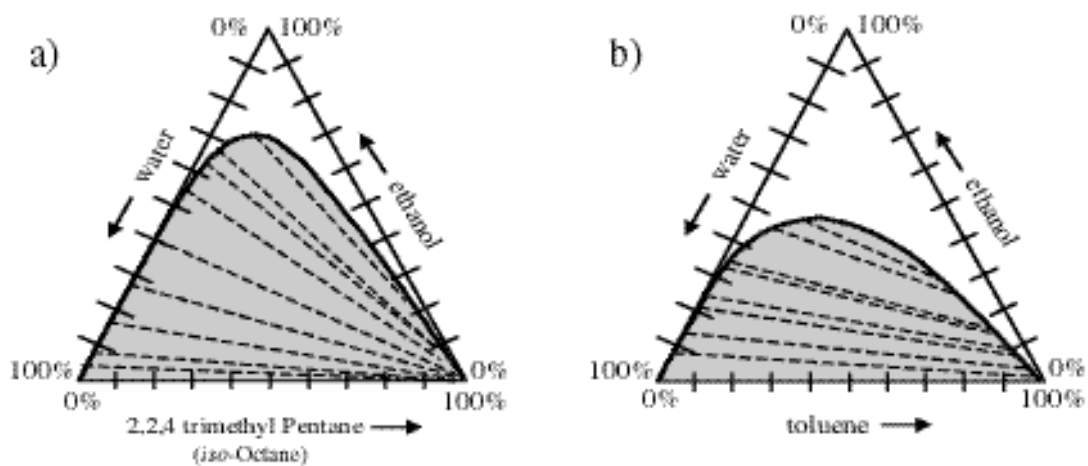
Figure 2-4. (a) Ternary-phase diagram for 2,2,4-trimethylpentane-ethanol-water system and (b) toluene-ethanol-water system at 25°C. Axes indicate mole percentages (adapted from Peschke and Sandler, 1995).
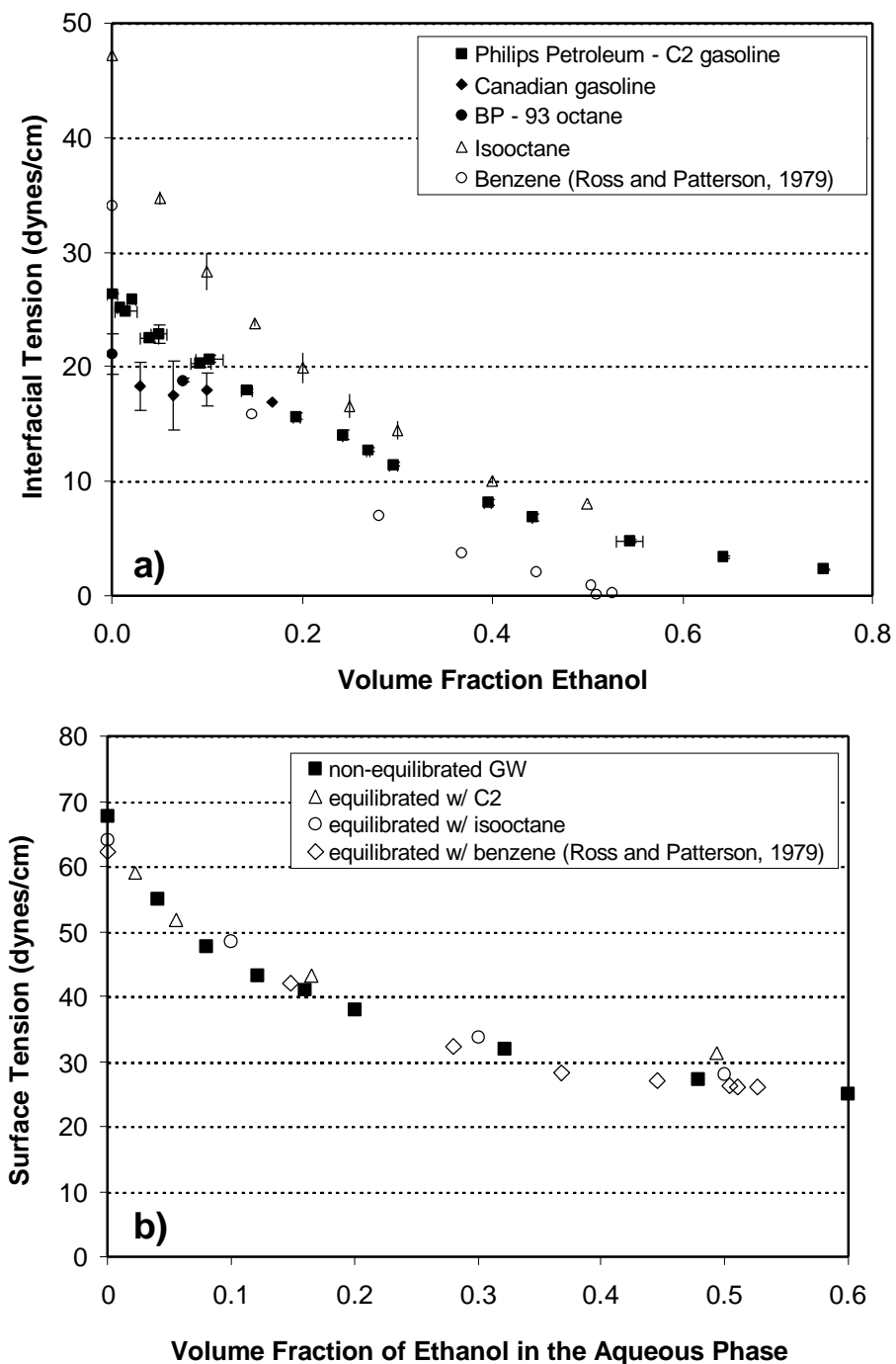
Figure 2-5. Interfacial and surface tensions of gasolines and organic chemicals in the presence of ethanol: (a) interfacial tension between organic and aqueous phases; (b) surface tension of water or water that was previously equilibrated with an organic phase. Data from Kowles and Powers (1997) except where noted.
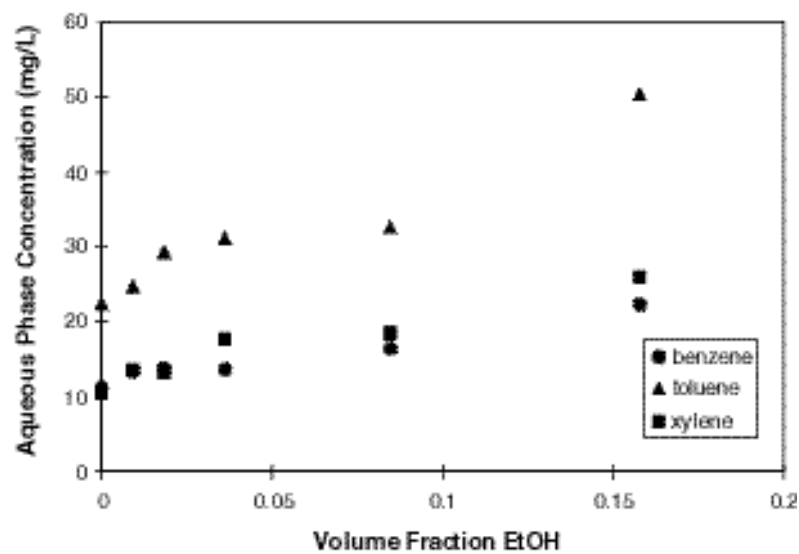
Figure 2-6. Concentration of BTX compounds in water equilibrated with a Brazilian gasoline containing 22% ethanol (data from Fernandes, 1997).
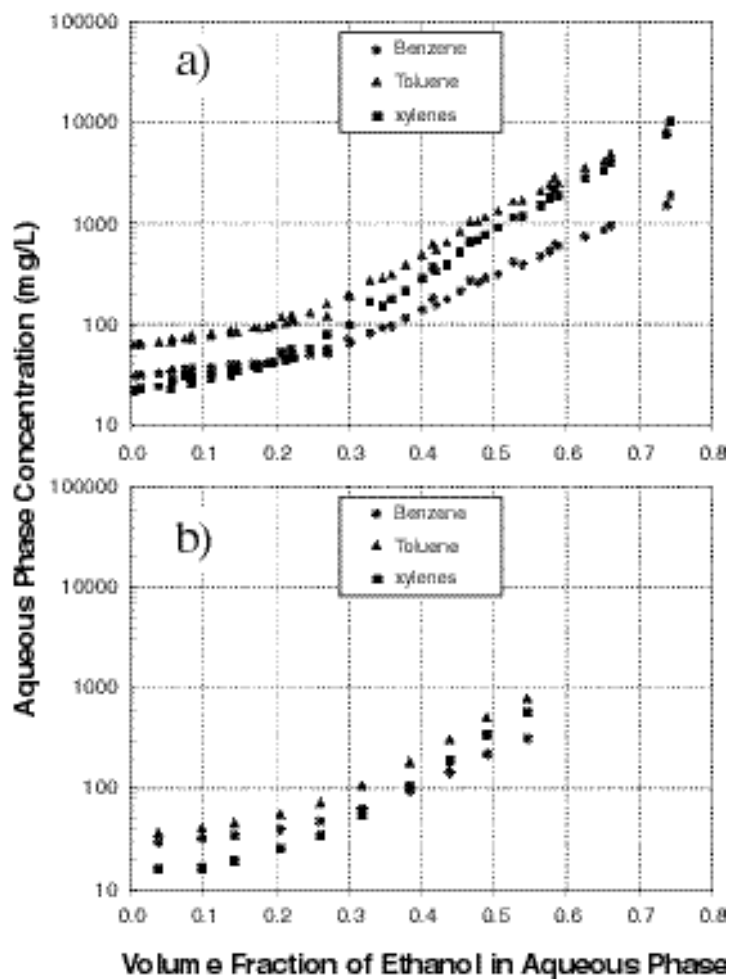
Figure 2-7. (a) Concentration of BTX compounds in water equilibrated with a certified California test gasoline from Philips Petroleum and (b) a generic ethanol-gasoline (purchased from a Gas Bar service station in Cornwall, Ontario, Canada ~3.4% ethanol by volume) (data from Heermann and Powers, 1998).
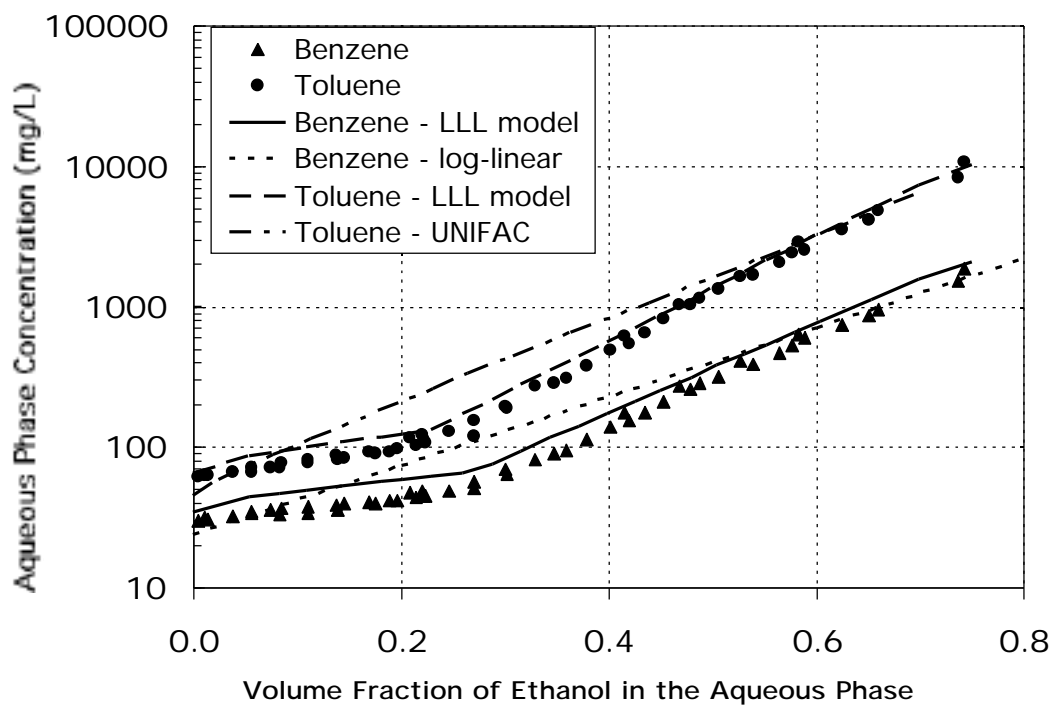
Figure 2-8. Prediction of benzene and toluene concentrations that had been equilibrated with C2 gasoline and additional ethanol. "LLL" (in legend) indicates the piecewise linear-log-linear cosolvency model (from Heermann and Powers, 1998).

(a) early development of miscible fingers as ethanol is depleted from the gasoline-water interface

(b) advanced development of miscible fingers

Explanation

gasoline still containing ethanol
less dense gasoline depleted of ethanol
horizontal arrows indicate diffusion/dispersion into and out of fingers
vertical arrows indicate direction of gasoline movement; less dense ethanol-depleted gasoline moves upwards while gasoline with higher ethanol content moves downward
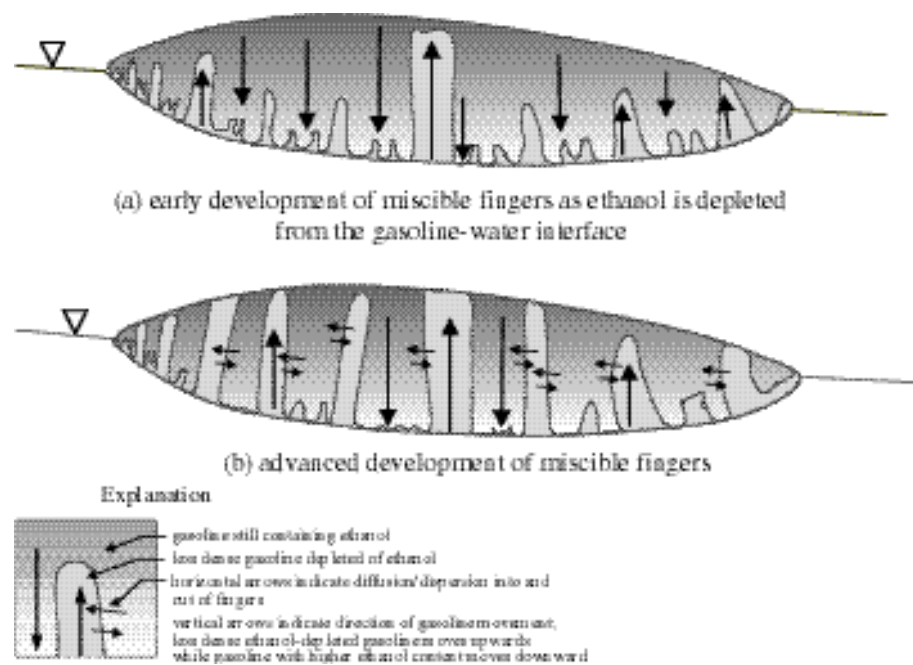
Figure 2-9. Conceptual drawing illustrating the transport of ethanol in a pool of gasoline at the water table via free convection.
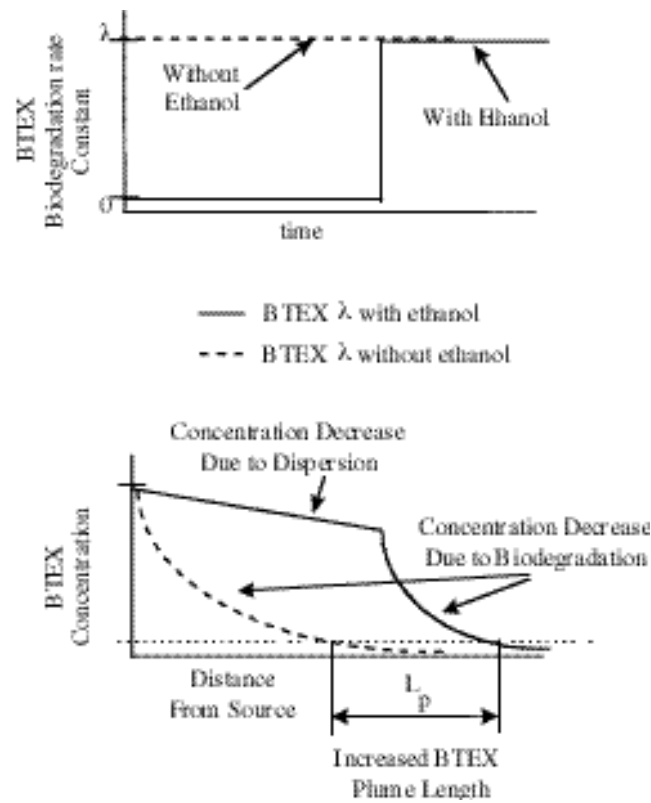
Figure 2-10. Schematic drawing of increased BTEX plume length due to the formation of a BTEX biodegradation lag time created by the presence of ethanol (from Malcolm Pirnie, Inc., 1998).
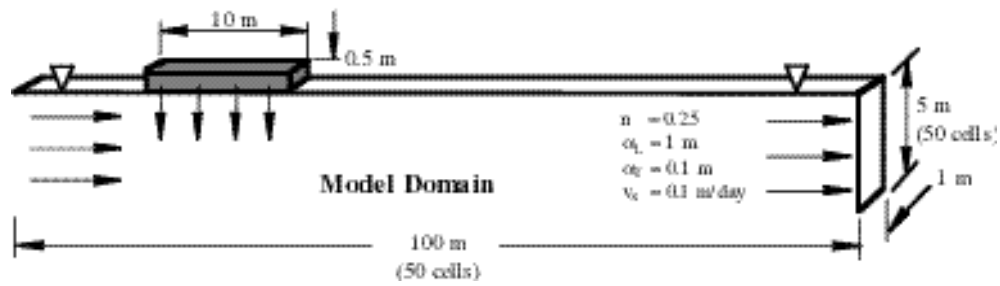
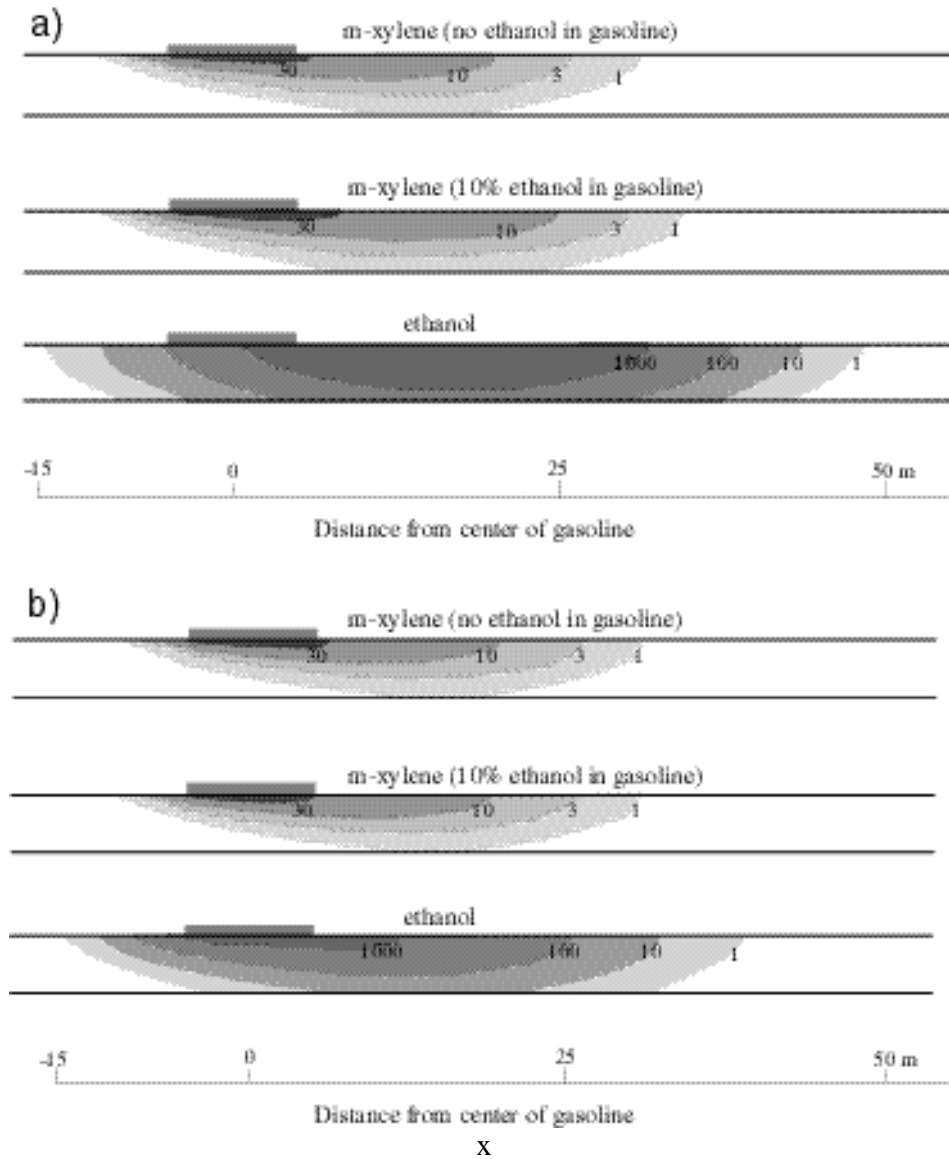**Figure 2-11. Domain used for gasoline dissolution and groundwater transport model (Heerman and Powers, 1996).**

Figure 2-12. Predicted concentration contours for m-xylene and ethanol dissolved from oxygenated gasoline under (a) local equilibrium conditions (kin = 0^{-3} m/s) and (b) mass-transfer rate-limited conditions (kin = 10^{-8} m/s). All concentrations are in mg/L. (time = 180 days) (Heermann and Powers, 1996).

Tables

Table 2-1. Potential impacts of ethanol in gasoline on the subsurface fate and transport of gasoline and gasoline constituents.

Process	Properties/mechanisms affected	Potential impact	Variables of importance

Unsaturated Zone:
• *Infiltration*
• *Spreading at the capillary fringe*
	• *Capillary forces—reduction in surface and interfacial tension*
	• *Effective permeabilities*
	  – *Volume changes as ethanol partitions into water*
	  – *Dehydration and cracking of clay strata*
		• *Size and shape of gasoline pool*
		• *Distribution of gasoline residuals in the unsaturated zone and periphery of the pool*
			• *Volume and duration of the spill event*
			• *Gasoline composition*
			• *Heterogeneity in mineral type, grain size, and water content*

Gasoline Source • *Leaching of chemicals into groundwater*	• *Equilibrium composition of the two phases* • *Mechanisms of transport of chemical species through the gasoline pool* • *Mass-transfer rates across the gasoline-water interface*	• *Concentrations of BTEX and ethanol at the source* • *Life span of the source*	• *Gasoline composition* • *Groundwater velocities* • *Length and depth of the gasoline pool* • *Presence of residual droplets of gasoline in the vicinity of the pool*
Aqueous Phase • *Transport of BTEX and ethanol to downgradient receptors*	• *Adsorption equilibria* • *Precipitation of gasoline droplets* • *Biodegradation rates and mechanisms*	• *Size and shape of contaminated groundwater plume*	• *All variables affecting groundwater flow* • *Concentrations of species at the source* • *Concentrations of electron acceptors* • *Organic content of mineral matrix* • *Ethanol concentration*

Table 2-2. Increased BTX concentration (%) in the aqueous phase equilibrated with C2 gasoline relative to estimated concentrations without any ethanol.[a]

Vol. fraction ethanol in aqueous phase (%)	Benzene (%)	Toluene (%)	Xylenes (%)
13.8	7.5	26	27
17.5	19	41	53

[a] *Data from Heermann and Powers, 1998.*

Appendix A
Cosolvency Mechanisms and Modeling

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Cosolvency Mechanisms and Modeling

A-1. Thermodynamic Equilibrium Conditions

Thermodynamic equilibrium conditions for nonaqueous phase liquids (NAPL) dissolution processes are defined by equal fugacities of a species i (f_i) in the NAPL (n) and aqueous phase (w) (Stumm and Morgan, 1981). Under isothermal conditions with a consistent reference state, equilibrium conditions can be redefined by equating the activity of each species between phases:

$$a_i^n = a_i^w \tag{A-1a}$$

$$\gamma_i^n x_i^n = \gamma_i^w x_i^w \tag{A-1b}$$

where, the activity, which defines the non-ideal behavior of the solute within a given phase, is given as $a_i = \gamma_i x_i$; x_i is a mole fraction, and γ_i is the activity coefficient. Many NAPLs, including standard formulation gasolines, are comprised of mixtures of similar types of organic chemicals and can, therefore, be assumed to be chemically ideal. Under ideal conditions, NAPL-phase activity coefficients are unity while activity coefficients for dilute concentrations of solute in the aqueous phase can usually be assumed to be constant (MacKay *et al.,* 1991). Thus, a linear relationship exists between mole fractions, x_i, of a species in the two phases. This linear relationship can be reduced to Raoult's law to estimate the equilibrium aqueous-phase concentration, C_i^{*w}, in terms of the pure liquid phase solubility, C_{s_i} (MacKay *et al.,* 1991):

$$C_i^{*w} = C_{s_i} x_i^n \tag{A-2}$$

Alternatively, the linear relationship can be represented with a NAPL-water partition coefficient, K_i^{nw}, to relate the mass concentration of a constituent in the organic phase to that in the aqueous phase:

$$K_i^{nw} = \frac{C_i^n}{C_i^{*w}} \tag{A-3}$$

Under ideal conditions, the partition coefficient is constant, making it relatively straightforward to estimate concentrations in the aqueous phase that would be in equilibrium with an organic phase.

A-2. Empirical Cosolubility Models

The empirical models for the solubility of hydrophobic organic compounds (HOCs) in non-ideal systems involve the use of both linear and log-linear equations. These equations were

originally used for the solubility of pharmaceuticals but have also been applied to environmental systems (Banerjee and Yalkowsky, 1988). In general, cosolvents in water generate a logarithmic increase in HOC solubility with increasing cosolvent concentration (Pinal *et al.,* 1990):

$$log(C_i^m) = log(C_{si}^w) + \sigma_s f^c \tag{A-4}$$

where C_i^m is the equilibrium concentration of HOC *i* in the cosolvent mixture, C_{si}^w is the solubility of HOC *i* in pure water, f^c is the volume fraction of the cosolvent in the aqueous phase, and σ_S is termed the *cosolvency power*. Examination of the limiting case (f^c=1) enables the cosolvency power to be estimated from experimental data:

$$\sigma_s = log \frac{C_i^c}{C_{si}^w} \tag{A-5}$$

where C_i^c is the solubility of *i* in the pure cosolvent. Although Equation (A-4) is typically applied in an empirical manner, it has a basis in thermodynamic principles. Thus, the cosolvency power can be estimated from the physicochemical properties of the solute and solvents:

$$\sigma_s = \frac{N\left(\gamma_{i:w}^e - \gamma_{i:c}^e\right)HSA}{2.3RT} \tag{A-6}$$

where *N* is Avagadro's number; γ^e is the interfacial energy ($J\ cm^{-2}$) between the solute (*i*) and water (*w*) or cosolvent (*c*); *HSA* is the solute's hydrophobic surface area (cm^2/molecule); *R* is the universal gas constant ($J\ mol^{-1}\ K^{-1}$); and *T* is the absolute temperature *(*K) (Yalkowski *et al.,* 1976).

Deviations from the log-linear cosolubility relationship (Equation [A-4]) have been observed in studies of the solubilization of non-polar drugs in a variety of cosolvents solutions (Rubino and Yalkowsky, 1987), polychlorinated biphenyls (PCBs) in water-miscible alcohols (Li and Andren, 1994), and BTEX species in gasoline-methanol-water systems (Poulson *et al.,* 1992). For short-chained alcohols, these deviations have been attributed to changes in the interactions between water and the cosolvent molecules (Rubino and Yalkowsky, 1987). At low ethanol volume fractions, ethanol molecules are partially segregated from water via hydration spheres; whereas at higher ethanol fractions, hydration is no longer a dominant solubilization process, and the HOC has access to both water and cosolvent molecules in approximate proportion to their volume fractions.

At cosolvent volume fractions less than between 0.1 to 0.2, hydration spheres largely confine cosolvent molecules (Banerjee and Yalkowsky, 1988). Based on results of a study of aqueous-ethanol solutions, Grunwald (1984) described the volume within such spheres as being in a state of reduced hydrogen bonding as a result of disruption of the water network by the cosolvent. This would lead to a reduction in the hydrophobic effect within the spheres and an increase in HOC solubility. In contrast, outside of the hydration spheres, hydrogen bonding between water molecules is increased, and both ethanol and HOC molecules are largely excluded as a result of the hydrophobic effect.

The influence of the formation of hydration spheres was demonstrated by Banerjee and Yalkowsky (1988) using toluene as the HOC, and propylene glycol and methanol as cosolvents. At low volume fractions of the cosolvent, the solubilization of toluene was found to increase linearly with increasing cosolvent volume fraction—a direct influence of the volume of the hydration spheres. As the volumes of the hydration spheres expand, they intersect and eventually encompass the entire aqueous phase. They postulate that the intersection of the hydration spheres occurs at the breakpoint observed between linear and log-linear relationships between aqueous-phase solubilities and cosolvent volume fractions.

Because the log-linear cosolubility models (Equations [A-4]–[A-6]) do not incorporate the influence of the hydration spheres on the mechanisms of solubilization, this equation is only valid at higher cosolvent concentrations. Incorporating the observed linear relation at lower cosolvent concentrations, two equations can be written to reflect differences in solubilization mechanisms at low versus high cosolvent concentrations (Banerjee and Yalkowsky, 1988).

$$C_i^m = \left(1 - \frac{f^c}{\beta}\right) C_i^w + f^c\, C_i^\beta \qquad \text{for } f^c < \qquad\qquad\text{(A-7a)}$$

$$ln\,C_i^m = \left(1 - \frac{f^c - \beta}{1 - \beta}\right) ln\,C_i^\beta + \left(\frac{f^c - \beta}{1 - \beta}\right) ln\,C_i^c \qquad for\, f^c \geq \beta \qquad\text{(A-7b)}$$

where β is the volume fraction of ethanol in the aqueous phase at the breakpoint between the two segments of the model, and C_i^β is the concentration of i in the cosolvent mixture at this ethanol volume fraction. These model equations are referred to as the linear/log-linear model.

A-3. Models for Estimating Activity Coefficients

An alternative approach to modeling the solubilities of HOCs in a cosolvent mixture is to employ a thermodynamic model to estimate activity coefficients of each component in each phase and to equate the chemical activities in each phase (Equation [A-1b]). Most of these models (Margules, *UNI*versal *QUA*si *C*hemical [UNIQUAC], Non-Random-Two-Liquid [NRTL]) require a substantial amount of experimental data to fit the model parameters (Smith and Van Ness, 1987). Of these, the UNIQUAC model is often used in multicomponent liquid-liquid equilibrium problems. In this model, statistical mechanics are used to include the effect of molecular structure on liquid activity coefficients, resulting in a basic equation that incorporates the influence of both the entropy effects associated with the size and shape of a molecule (the combinatorial part) and the molecular interactions of functional groups between the different molecules (the residual part) (Henley and Seader, 1981):

$$\ln\gamma_i = \ln\gamma_i^c + \ln\gamma_i^r \qquad\qquad\qquad\text{(A-8)}$$

Here, superscripts *c* and *r* indicate the combinatorial and residual contributions, respectively, and subscript *i* refers to the chemical solute (Fredenslund *et al.,* 1975). The parameters γ_i^c and γ_i^r are determined from properties of the pure species, and experimental binary equilibrium data for

each pair of species. These expressions are dependent on the molecular volume, molecular surface area, and binary interactions among the different molecules.

The UNIQUAC Functional-group Activity Coefficients (UNIFAC) model was developed with the same theoretical basis as UNIQUAC although the necessary parameters are estimated from the number and type of functional groups that comprise the chemical species. Because this model does not require extensive data, it is more easily implemented than UNIQUAC although additional errors are introduced by estimating rather than measuring some of the parameters. This model is based on the premise that surface volume and area properties of the individual functional groups that comprise a molecule can be summed to estimate properties of the entire molecule (Fredenslund *et al.,* 1975). The group parameters are tabulated for numerous functional groups in most standard thermodynamics textbooks (for example, Smith and Van Ness, 1987). An additional parameter, describing interactions among each of the functional groups is also required for the UNIFAC model. These group interaction parameters have been determined from a large database of experimental data and have been updated numerous times since the initial development of the UNIFAC model. The most recent corrections and additions were made in 1991 (Hansen *et al.,* 1991).

The difficulty in utilizing UNIFAC for complex systems is the need to understand the composition and structure of all components within the system. This is typically not feasible with complex petroleum hydrocarbons. Perry and Chilton (1973) suggest the use of "pseudocomponents" to lump many components into one with average properties. Peters and Luthy (1993) described a coal tar as a pseudocomponent in an assessment of phase equilibria for ternary coal tar-water-solvent systems. They found that this approach was useful for analyzing the effect of polar solvents added to increase coal tar solubilization.

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Appendix B
Modeling Interphase Mass-transfer Processes

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B-1. Interphase Mass Transfer

Interphase mass transfer describes the net movement of a substance across an interface dividing two phases in response to a chemical thermodynamic disequilibrium between those phases. If changes in concentration occur abruptly across the interface and the two phases are relatively homogeneous except near the interface, the flux, or rate of mass transfer per unit-area of the interface, can be expressed as a product of a mass-transfer coefficient and a concentration difference (Cussler, 1984)

$$N_i = k_i \cdot (C_i^{*a} - C_i^{a})$$ (B-1)

where N_i is the flux of compound i, k_i is the mass-transfer coefficient, C_i^{a} and C_i^{*a} are the concentrations of compound i in phases a and the concentration of i that would be in equilibrium with the concentration in phase b, respectively. This equilibrium concentration is often defined by a partition coefficient ($K_i^{a,b}$):

$$C_i^{a} \approx K_i^{a,b} C_i^{b}$$ (B-2)

Thus, when $C_i^{a} = C_i^{a}*$, the net flux of compound i across the interface is 0. Within the present discussion, the two phases consist of a non-aqueous phase liquid (NAPL), designated by the superscript n and an aqueous phase, designated by the superscript w (for water*). Also, for brevity, interphase mass transfer is referred to more simply as mass transfer.

B-2. Estimating the Mass-transfer Coefficient

A number of methods exist to estimate the mass-transfer coefficient. Some of these are empirical correlations derived using dimensional analysis and experimental measurements. These are typically developed for specific geometries, such as NAPL entrapped as residual blobs or ganglia within a porous medium and subject to a uniform flow field (for example, Hunt *et al.,* 1988; Powers *et al.,* 1992, 1994). Others, such as the film theory and boundary layer theory are based upon physical models of the interface (Cussler, 1984).

A pool of NAPL, as in the case of a gasoline spill, generally provides a boundary condition for modeling the transport of aqueous-phase contaminants with the groundwater flow (Figure B-1). Two approaches can be used to quantify the input of contaminants from the gasoline source to the groundwater through interphase mass-transfer processes. A first type of boundary condition can be used to stipulate the concentration, or a second type of boundary condition can be developed to specify the flux of the organic species between phases.

Several researchers have found that a first-type boundary condition equating the concentration at the boundary to the solubility of the organic species comprising the single-component NAPL is adequate (Hunt *et al.,* 1988; Johnson and Pankow, 1992; Pearce *et al.,* 1994; Voudrais and Yeh, 1994; Chrysikopoulos, 1995). This boundary condition can be written as:

$$C^w(x,z) = C^{w*} @ z = 0, 0 < x < l, \tag{B-3}$$

With a single-component NAPL, the composition of the LNAPL does not change significantly with time, and an analytical solution to the transport equation can be employed. The more complex case of a multicomponent NAPL has only recently been considered (Holman and Javandel, 1996). They still assumed that equilibrium is achieved at the boundary but incorporated diffusion of the hydrophobic organic compounds (HOCs) through the organic phase as a limitation of the total mass-transfer rate. In the assumed stagnant gasoline pool, diffusion would be the predominant transport mechanism.

A flux term has been utilized to describe interfacial mass-transport processes of an organic species between residual NAPL blobs and the aqueous phase. The mass-transfer flux is generally described with a linear driving force (Equation B-1). In general, it is assumed that the concentrations in each phase right at the interface are in equilibrium. A couple of different mass-transfer theories can be used to estimate the mass-transfer coefficient.

Previous models of mass transfer from NAPL lenses have assumed that mass-transfer limitations are controlled by the flux of the solute away from the interface via advection and hydrodynamic dispersion by the groundwater (Johnson and Pankow, 1992; Voudrias and Yeh, 1994; Hunt *et al.*, 1988). This physical situation most closely follows that of penetration theory (Cussler, 1984).

Penetration theory assumes that the mass transfer across an interface is controlled by the diffusive flux away from the interface. Figure B-2 illustrates changes in concentration as a result of the mass transfer from a NAPL to a flowing aqueous liquid. This is adapted from Cussler (1994) although the original figure contained a vapor phase in place of the NAPL. Using the geometry shown in Figure B-2 and assuming (1) a constant concentration in the NAPL over the length *L* of the interface; (2) an aqueous phase of infinite vertical extent; (3) laminar flow parallel to the interface, the steady-state mass transfer could be described by the following differential equation:

$$u_{max} \frac{\partial C_i^w}{\partial x} = D \frac{\partial^2 C_i^w}{\partial z^2} \tag{B-4}$$

where D is the diffusion coefficient of compound i in water, u_{max} is the maximum velocity of flow, and C_i^w is the concentration of compound i in the aqueous phase. It is assumed that u_{max} occurs parallel to the interface and is constant except immediately adjacent to the interface. Solving Equation (B-4) for the following boundary conditions:

$$C_i^w(x, z = \quad) = 0$$

$$C_i^w(x, z = 0) = \frac{C^n}{K_i^{n,w}} \qquad 0 < x < l \tag{B-5}$$

$$C_i^w(x = 0, z) = 0$$

yields a solution from which the steady-state flux across the interface can be derived

$$N_i = \sqrt{\frac{D \, u_{max}}{\pi \, x}} \quad \frac{C_i^n}{K_i^{n,w}} - C_i^w \tag{B-6}$$

The mass-transfer coefficient for steady state would then be equal to (Cussler, 1984):

$$k_i = \sqrt{\frac{4 \, D \, u_{max}}{\pi \, L}} \tag{B-7}$$

Extending this to describe mass transfer in a porous medium requires several modifications. In a porous medium, spatial variations in velocity within the pores, tortuous flow around the solid phase, and divergence of flow as a result of larger-scale heterogeneities generate transverse dispersion. Considering only transverse dispersion in the vertical direction, the vertical component of the hydrodynamic dispersion tensor is equal to the sum of the molecular diffusion (divided by the tortuosity, τ_z) and the vertical component of the dispersion tensors (Bedient *et al.,* 1994). Furthermore, as a first approximation, the components of the dispersion tensor can be linearly related to the horizontal velocity by a proportionality constant, in this case $_z$, the vertical dispersivity

$$D_z = \frac{D}{\tau_z} + \alpha_z v_x \tag{B-8}$$

Finally, accounting for the volume fraction of the solid phase and not yet considering NAPL, the mass-transfer coefficient would be computed as follows:

$$k_i = \varepsilon \sqrt{\frac{4D_z \, v_x}{\pi \, L}} \tag{B-9}$$

where ε is the porosity of the porous medium. Multiplying this by the difference in concentration between the NAPL and aqueous phases, the net steady-state flux would be then be equal

$$N_i = \varepsilon \sqrt{\frac{4D_z \, v_x}{\pi \, L}} \quad \bullet \quad \frac{C_i^n}{K_i^{n,w}} - C_i^w \tag{B-10}$$

This approach has been applied in recent years for estimating the dissolution from pools of NAPL less dense than water (Hunt *et al.,* 1988; Voudrias and Yeh, 1994) as well as pools of NAPL with specific gravities greater than unity (Anderson *et al.,* 1992; Johnson and Pankow, 1992; Pearce *et al.,* 1994).

Holman and Javandel (1996) extended the complexity of the mass-transfer problem in a two-dimensional cross section to include time-dependent mass transfer and rate limitations caused by diffusional resistances in the NAPL. A system of two differential equations was solved. The first of these equations described the diffusive flux of HOC through the NAPL:

$$\frac{\partial C_i^n}{\partial t} = D_i^n \left(\frac{\partial^2 C_i^n}{\partial x^2} + \frac{\partial^2 C_i^n}{\partial z^2} \right) \qquad\qquad 0 \le x \le l,\ 0 \le z \le h_0,\ t > 0 \qquad\qquad \text{(B-11)}$$

while the second described advective-diffusive transport of the solute through the aqueous phase:

$$\frac{\partial C_i^w}{\partial t} = D_x^w \frac{\partial^2 C_i^w}{\partial x^2} + D_z^w \frac{\partial^2 C_i^w}{\partial z^2} - u_x \frac{\partial C_i^w}{\partial x} \qquad\qquad 0 \le x \le \infty,\ -h \le z \le 0,\ t > 0 \qquad\qquad \text{(B-12)}$$

Here, D_i^n is the diffusion coefficient of compound *i* in the NAPL, and D_x^w and D_z^w are the aqueous-phase coefficients of hydrodynamic dispersion. (It should be noted that some expressions have been altered from the original published work in order to create consistency between equations presented here.)

Boundary conditions for the NAPL consisted of zero flux at the upper and lateral boundaries and a the following conditions at the groundwater interface which served to couple Equations (B-11) and (B-12)

$$C_i^w = K_i^{w,n} C_i^n \qquad (0 \le x \le l,\ z = 0,\ t > 0)$$

$$\frac{D_z^w \rho^w}{M^w} \frac{\partial C_i^w}{\partial z} = \frac{D_i^n \rho^n}{M^n} \frac{\partial C_i^n}{\partial z} \qquad (0 \le x \le l,\ z = 0,\ t > 0) \qquad\qquad \text{(B-13)}$$

The first of these equations equates the chemical activities at the interface, and the second equates the molar flux leaving the NAPL with that entering the groundwater. The appearance of expressions for the densities, ρ^w and ρ^n, and molecular weights, M^w and M^n, of the bulk fluids in Equation (B-13) reflect the authors' use of mole fraction as a unit of concentration. Zero-flux boundary conditions are applied to the groundwater at the base of the aquifer, the upstream boundary, and at the water table where the NAPL does not exist.

The analytical solution derived from the differential equations and boundary and initial conditions is a tremendous advancement from the steady-state approach used previously (Hunt et al., 1988; Voudrias and Yeh, 1994; Anderson *et al.,* 1992; Johnson and Pankow; 1992; Pearce *et al.,* 1994). However, implementation of the solution is very difficult because the solution is presented in Laplace space and the inverse transform must be performed numerically.

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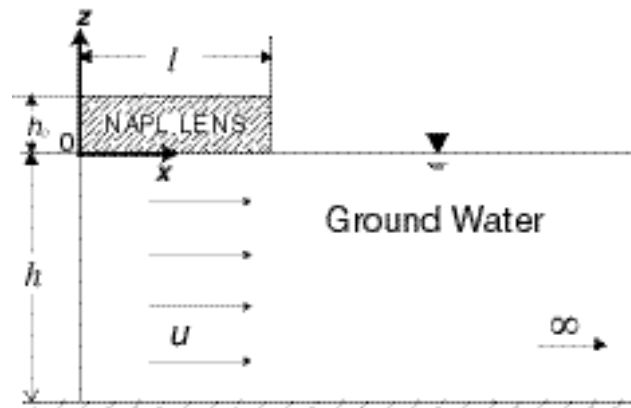
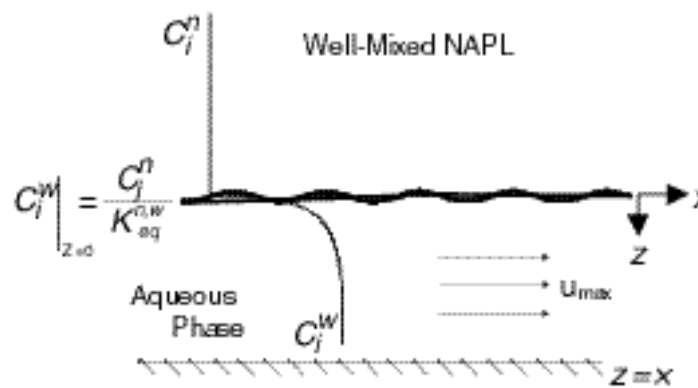**Figure B-1. Typical geometry used for modeling teaching from an LNAPL pool.**

Figure B-2. Illustration for Penetration theory (adapted from Cussler, 1997).